

# The American Mineralogist

## Journal of the Mineralogical Society of America

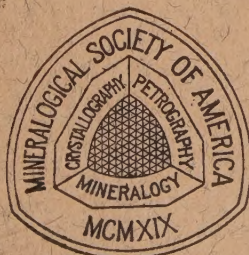
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Nos. 1 and 2

### Contents

Kyanite, andalusite, and sillimanite in the schist in Boehls Butte quadrangle, Idaho.....	Anna Hietanen	1
On the genesis of residual kaolins.....	L. B. Sand	28
Amblygonite, cassiterite, and associated minerals from Cáceres, Western Spain.....	Max Weibel	41
Solvents and solutes for the preparation of immersion liquids of high index of refraction.....	Robert Meyrowitz	49
Faces and habits of diamond type crystals.....	G. A. Wolff	60
Tubular morphology of some Brazilian kaolins.....		
Y. Stourdze Visconti, B. N. F. Nicot, and E. Goulart de Andrade. Electron micrographs by A. C. Villanova.....		67
Bastnaesite, an accessory mineral in the Redstone granite from Westerly, Rhode Island.....	William Lee Smith and Evelyn A. Cisney	76
Abernathyite, a new uranium mineral of the metatorbernite group.....		
M. E. Thompson, Blanche Ingram, and E. B. Gross		82
Allevardite, a swelling double-layer mica mineral.....	G. W. Brindley	91
Osumilite, a new silicate mineral, and its crystal structure.....	Akiho Miyashiro	104
Oscillating-heating x-ray diffractometer studies of clay mineral dehydroxylation.....	E. J. Weiss and Richards A. Rowland	117
Studies of uranium minerals (XIX): Rutherfordine, diderichite, and clarkeite.....	Clifford Frondel and Robert Meyrowitz	127
The empirical unit cell contents of the friedelite family.....	Max H. Hey	134
Notes and news: A notable centenary in American mineralogy: Samuel Lewis Penfield, 1856-1906.....	Michael Fleischer	139
Paragonite in the schist of Glebe Mountain, Southern Vermont.....		
John L. Rosenfeld		144
Antigorite: Superlattice and structural formula.....	J. Zussman	148
Novacekite from the Wichita Mountains, Oklahoma.....	W. T. Huang	152
An unusual palagonite tuff.....	Duncan McConnell	153
New occurrences of native selenium.....		
M. E. Thompson, Carl Roach and William Braddock		156
Age determination of zircon crystals from Ceylon.....		
David Gottfried, F. E. Senftle, and C. L. Waring		157
Book reviews.....		162
New mineral names.....		163



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# THE AMERICAN MINERALOGIST

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## KYANITE, ANDALUSITE, AND SILLIMANITE IN THE SCHIST IN BOEHLS BUTTE QUADRANGLE, IDAHO\*

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### ABSTRACT

Kyanite, andalusite, and sillimanite are found together in the cordierite-bearing mica schist of the Prichard formation of the Precambrian Belt series exposed in the Boehls Butte quadrangle in the southern part of the Idaho panhandle. Microscopic studies of this schist suggest that the following inversions took place: (1) sillimanite→kyanite, (2) sillimanite→andalusite, (3) kyanite→andalusite, (4) kyanite→sillimanite, (5) andalusite→sillimanite. These inversions can be in part related to the fluctuation of temperature and stresses during the complex regional and thermal metamorphism to which the schist was subjected. In some thin sections all three modifications occur side by side, suggesting that they were crystallized close to the physical-chemical conditions in which all three may exist together. The association of epidote and plagioclase (An<sub>36</sub>) in the calcium-rich beds of the same area suggests that the temperature during the crystallization was close to 400° C.

### CONTENTS

	Page
Abstract.....	1
Introduction.....	2
General geology.....	3
Occurrence of the three aluminum silicates together.....	3
Kyanite-andalusite-sillimanite-cordierite gneiss on Smith Ridge.....	5
Description of the gneiss.....	5
Optical properties of the minerals in the gneiss.....	5
Chemical composition of the minerals and the gneiss.....	7
Relation of the aluminum silicates in the gneiss.....	8
Other occurrences.....	9
Andalusite-kyanite schist on the North Fork of Clearwater River.....	10
Minerals in the schist.....	10
Relation of the aluminum silicates in the schist.....	10
Continuation of the schist layer.....	12
Kyanite-andalusite schist in the Goat Mountain area.....	14
Minerals in the schist at Goat Mountain.....	15
Chemical composition of kyanite and andalusite.....	15
Relation of the aluminum silicates in the schist at Goat Mountain.....	17
"Sillimanite" gneiss.....	17

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Stauroilite-bearing schist .....	19
Sillimanite-kyanite-andalusite schist west of Goat Mountain .....	20
Summary of the alterations involving the aluminum silicates .....	21
Relation of the inversions of the aluminum silicates to the sequence of geologic events .....	22
Temperature and pressure of the inversions sillimanite $\rightleftharpoons$ kyanite $\rightleftharpoons$ andalusite .....	25
Conclusion .....	26
References .....	27

## Introduction

The three aluminum silicates—kyanite, andalusite, and sillimanite—occur together in the schist in Boehls Butte quadrangle and in an area

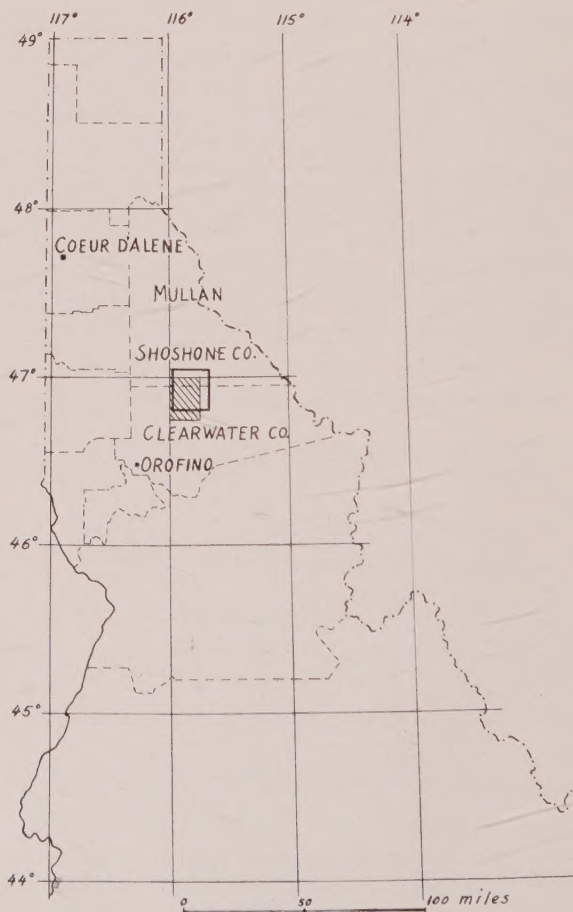


FIG. 1. Location of the area in Idaho. The area under discussion is surrounded with a heavy line. Boehls Butte quadrangle is shaded.



north of it. Boehls Butte quadrangle is situated in the southern part of the Idaho panhandle about 40 miles south of the Coeur d' Alene silver mining district (Fig. 1), in Clearwater and Shoshone Counties. The main rock type in this quadrangle is a folded coarse-grained mica schist belonging to the Prichard formation of the Precambrian Belt series. Quartzites and schists probably of the Burke, Revett, St. Regis, and Wallace formation of the Belt series are exposed in the southern part of the quadrangle, but these rocks do not contain more than possibly one of the aluminum silicates and therefore are not discussed in this paper. The mapping of this quadrangle was started during the summer of 1951 and is not yet completed. At the present stage of study, it is impossible to say how prevalent similar kyanite-andalusite-sillimanite-bearing schists are in the nearby areas, or whether they are confined entirely to the Prichard formation. The localities of the collected specimens, which contain all three modifications of  $\text{Al}_2\text{SiO}_5$ , are widely distributed in the Boehls Butte quadrangle and in an area just north of it (Fig. 2), suggesting that the occurrence of these minerals is a regional rather than a local feature.

### General Geology

The Prichard formation in the Boehls Butte quadrangle consists of a highly metamorphosed bedded and folded mica schist with a fairly pure white to gray quartzite, more than 1000 feet thick, close to the middle of the formation. In the lower and upper schistose members the thin quartzitic layers are interbedded with more micaceous layers. The thickness of various beds ranges from a few millimeters to several meters, the thinly bedded schist and quartzite being dominant. In the micaceous layers, huge muscovite and light-brown biotite flakes give a glittering yellowish-brown luster to the cleavage surfaces. With a few exceptions, the cleavage parallels the bedding. Numerous small garnet amphibolite bodies and a few larger anorthosite bodies, both with mainly concordant contacts, occur in this schist. The schist and quartzite are moderately folded and faulted. The general strike of the beds is  $\text{N } 45^\circ\text{--}70^\circ \text{ W}$ . Dips of  $15^\circ$  to  $45^\circ$  are common. The major fold axis trends about  $\text{N } 70^\circ \text{ W}$  and plunges  $5^\circ$  to  $25^\circ$  either to the east or to the west. Some outcrops show a strong lineation (wrinkling of  $s_1$ ) and minor folding around an axis that trends about  $\text{N } 25^\circ \text{ E}$ .

### Occurrence of the Three Aluminum Silicates Together

Kyanite, andalusite, and sillimanite occur in several localities in the mica-rich beds of the Prichard formation. Most of the schist carrying these three minerals is close to metasomatic anorthosite bodies (Fig. 2).





and 954, Fig. 2), and one northwest of Goat Mountain (1368) are described in detail.

*Kyanite-andalusite-sillimanite-cordierite gneiss on Smith Ridge*

The schist along Smith Ridge north of the anorthosite exposed at Boehls and along the river is mainly thin-bedded biotite schist with garnet-bearing layers. Small sills of gabbro and garnet amphibolite occur in the schist parallel to the bedding. Some of these bodies are only about 10 cm. thick and 2 to 3 meters long and were probably formed by replacement. Several large boulders of kyanite-andalusite-sillimanite-cordierite gneiss were found on the south slope of the ridge close to its top (912, Fig. 2). No outcrops were found in this locality, but the analogy with similar occurrences to the north and south suggests that the gneiss is a layer in the garnet-biotite schist.

Description of the gneiss

The kyanite-andalusite-sillimanite-cordierite gneiss is light bluish gray and coarse-grained. The alignment of minerals is less pronounced than in the surrounding schist. White grains of andalusite and kyanite are easily visible against the mixture of brown biotite and light grayish cordierite (Pl. 1a). Andalusite occurs as large rounded nodules or as individual large grains. Kyanite occurs as white prisms ranging from 1 to 15 mm. in length.

The microscopic study shows that this rock consists of abundant cordierite (about 37 per cent), biotite, and plagioclase, with less quartz, andalusite, sillimanite, corundum, kyanite and sericitic mica (Pl. 1b). The cordierite occurs in dull round grains that contain small sericite and some tiny sillimanite inclusions mainly parallel to the cracks and along the borders. Also there is some pinitization along the borders.

The biotite flakes, ranging from 1 to 2 mm. in length, are very light brown and show a crude alignment. The three aluminum silicates tend to occur in clusters. Study under the microscope indicates that many of the white andalusite nodules appear to contain kyanite and sillimanite.

Optical properties of the minerals in the gneiss

The indices of refraction of the three aluminum silicates in the gneiss on Smith Ridge are shown in Table 1. They seem to be practically the same as those commonly reported for these minerals.

The indices of refraction of the cordierite are  $\alpha = 1.530 \pm 0.001$ ,  $\beta = 1.535 \pm 0.001$ ,  $\gamma = 1.538 \pm 0.001$ ; the cordierite is biaxial negative with  $2V = 84.5^\circ$ . The pleochroism of biotite is Z pale brown and X yellowish; the indices of refraction are  $\alpha = 1.558 \pm 0.001$ ,  $\beta = 1.601 \pm 0.001$ ,  $\gamma = 1.601$

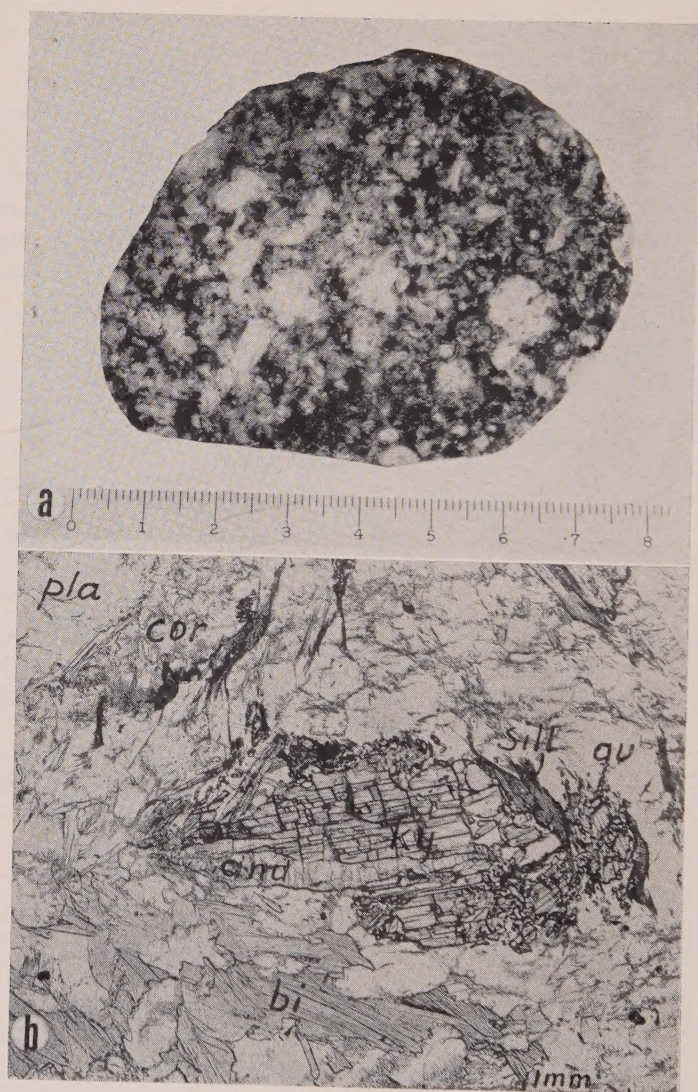


PLATE 1

- a.* Polished hand specimen of kyanite-andalusite-sillimanite-cordierite gneiss from Smith Ridge (912), Boehls Butte quadrangle. The white minerals are andalusite and kyanite.
- b.* Photomicrograph of the same rock as in *a* (912). ky=kyanite, and=andalusite, sill=sillimanite, cor=cordierite, bi=biotite, pla=plagioclase, qu=quartz, +Nicols.



TABLE 1. INDICES OF REFRACTION OF KYANITE, ANDALUSITE, AND SILLIMANITE IN SCHIST FROM SMITH RIDGE, BOEHLS BUTTE QUADRANGLE (912, FIG. 2)

Kyanite	Andalusite	Sillimanite
$\alpha=1.7125\pm0.001$	$\alpha=1.631\pm0.001$	$\alpha=1.654\pm0.001$
$\beta=1.722\pm0.001$	$\beta=1.637\pm0.001$	$\beta=1.656\pm0.001$
$\gamma=1.727\pm0.001$	$\gamma=1.642\pm0.001$	$\gamma=1.677\pm0.001$

$\pm 0.001$  with  $2V=0^\circ$ . X-ray powder photographs of this cordierite and biotite, made by F. A. Hildebrand of the Geological Survey, show typical cordierite and biotite patterns.

### Chemical composition of the minerals and the gneiss

Kyanite, cordierite, and biotite were separated by means of heavy liquids and analyzed chemically. Their composition and specific gravities are shown in Table 2.

The composition of kyanite is practically the same as that of the

TABLE 2. CHEMICAL ANALYSES OF KYANITE, CORDIERITE, AND BIOTITE FROM THE KYANITE-ANDALUSITE-SILLIMANITE-CORDIERITE GNEISS, FROM SMITH RIDGE, BOEHLS BUTTE QUADRANGLE (912, FIG. 2)

	Kyanite <sup>1</sup> (sp. gr. >3.3)		Cordierite <sup>1</sup> (sp. gr. 2.583-2.603)			Biotite <sup>2</sup> (sp. gr. 2.872-2.891)			
	Weight per cent	Molec- ular equiv- alent	Weight per cent	Molec- ular equiv- alent	Ratio	Weight per cent	Molec- ular equiv- alent		Number of atoms
SiO <sub>2</sub>	35.84	5944	49.46	8202	5	39.29	6541	Si	5.49
TiO <sub>2</sub>	0.01	1	0.01	1		0.58	72	Al	2.51
Al <sub>2</sub> O <sub>3</sub>	63.48	6330	33.58	3292	3301	21.06	2064	Al	0.96
Fe <sub>2</sub> O <sub>3</sub>	0.22	14	0.14	9	2	0.30	19	Ti	0.05
FeO	0.08	11	2.12	295		5.81	809	Fe	0.03
MnO	0.00		0.08	11		0.04	6	Fe	0.68
MgO	0.41	102	12.06	2991	3302	19.13	4744	Mn	0.01
CaO	0.00		0.03	5		0.00		Mg	3.97
Na <sub>2</sub> O	0.00		0.14	23		0.33	53	Ca	0.00
K <sub>2</sub> O	0.08	8	0.30	32		8.60	913	Na	0.09
P <sub>2</sub> O <sub>5</sub>	0.00		0.00					K	1.52
F						0.08	42	H	4.36
H <sub>2</sub> O—	0.01	6	0.10	55		0.07	39	F	0.03
H <sub>2</sub> O+	0.15	83	1.71	949		4.69	2603	O	24.0
	100.27		99.73			99.98			24.00
						—O 0.03			
						99.95			

<sup>1</sup> Lucile N. Tarrant, *analyst*.

<sup>2</sup> Lee C. Peck, *analyst*.

kyanite in the schist at Goat Mountain (Table 4). The only differences are somewhat larger amounts of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the kyanite along Smith Ridge. The higher percentage of  $\text{MgO}$  in the kyanite at Smith Ridge may be due to the impurities; the two kyanites are optically identical.

The ratio  $(\text{MgO} + \text{FeO} + \text{CaO}) : \text{Al}_2\text{O}_3 : \text{SiO}_2$  in the cordierite is 2:2:5 and the ratio  $\text{FeO} : \text{MgO}$  is 1:10. Thus, this cordierite is an almost pure magnesium member of the naturally occurring cordierites (Folinsbee, 1941). The chemical composition and the indices of refraction are close to those of a cordierite from Attu, Finland (Pehrman, 1932), but the optic sign is negative, whereas that of the cordierite from Attu is positive. Folinsbee (1941) has suggested that the optic angle would tend to increase with decrease in alkali content. The properties of the cordierite on Smith Ridge accord with this suggestion.

The analysis of biotite shows that this mineral is rich in magnesium and aluminum. The formula calculated (Table 2, number of atoms) is  $(\text{OH})_4\text{H}_{0.4}\text{K}_{1.6}(\text{Mg}, \text{Fe})_{4.7}\text{Al} \cdot \text{Al}_{2.5}\text{Si}_{5.5} \cdot \text{O}_{20}$ . This differs from the ideal formula  $(\text{OH})_4\text{K}_2(\text{Mg}, \text{Fe})_6\text{Al}_2\text{Si}_6\text{O}_{20}$  mainly in a larger amount of Al. Part of the Si in the  $\text{AlSi}_3\text{O}_{10}$  sheets is substituted by Al, which also substitutes for a part of the Mg and Fe atoms in the structure. The substitution of Al for Si and Mg is common in eastonite, the ideal formula of which is  $(\text{OH})_4\text{K}_2\text{Mg}_5\text{Al} \cdot \text{Al}_3\text{Si}_5\text{O}_{20}$ . The substitution of Al for Si in the biotite from Smith Ridge puts that biotite well between these two end members. The Mg:Fe ratio is 6:1 and there is only a little fluorine.

Table 3 shows the chemical, measured, and calculated mineralogical composition of the kyanite-andalusite-sillimanite-cordierite gneiss from Smith Ridge. The thin sections do not show calcite. Most of the  $\text{Al}_2\text{SiO}_5$  is kyanite. The norm shows 26.33 per cent excess of  $\text{Al}_2\text{O}_3$  and 23.07 per cent  $\text{MgSiO}_3$ . Plagioclase ( $\text{An}_{17}$ ) is richer in albite than this mineral in the adjacent garnet-biotite schist, where it is generally about  $\text{An}_{25}$ . Thus, this gneiss layer is exceptionally poor in calcium and rich in magnesium and aluminum.

#### Relation of the aluminum silicates in the gneiss

The relation between the three aluminum silicates is not always clear. There are two types of sillimanite, brownish fibrous nodules and colorless needles (Fig. 3). The brownish nodules have colorless needles in their borders, and fresh kyanite is found next to the nodules. The colorless needles occur also around andalusite and kyanite, suggesting that these needles were formed at the expense of kyanite and andalusite. Most of the andalusite occurs as fresh large grains showing only slight strain shadows. However, some kyanite is surrounded by small grains of strained andalusite (cf. Pl. 4b) suggesting a transformation kyanite



TABLE 3. CHEMICAL AND MINERALOGICAL COMPOSITION AND NORM OF THE KYANITE-ANDALUSITE-SILLIMANITE-CORDIERITE GNEISS FROM SMITH RIDGE, BOEHLS BUTTE QUADRANGLE

	Weight per cent <sup>1</sup>	Mol.	Norm		Mode	
SiO <sub>2</sub>	48.20	7993	qu	12.80	quartz	3.20
TiO <sub>2</sub>	0.14	17	or	13.73	plagioclase (An <sub>17</sub> )	15.65
Al <sub>2</sub> O <sub>3</sub>	32.54	3190	ab	14.09		
Fe <sub>2</sub> O <sub>3</sub>	0.23	14	an	2.70	biotite	25.14
FeO	2.24	312	cor	26.33	sericite	0.20
MnO	0.05	7	en	23.07	cordierite	37.10
MgO	9.30	2306	fs	3.80	kyanite	17.86
CaO	0.84	150	ap	0.03	andalusite	
Na <sub>2</sub> O	1.66	268	il	0.25	sillimanite	
K <sub>2</sub> O	2.32	246	mt	0.32	(calcite)	(0.50)
P <sub>2</sub> O <sub>5</sub>	0.01	1	cal	0.50	apatite	0.02
CO <sub>2</sub>	0.22	50		97.62		99.67
H <sub>2</sub> O—	0.12	67	H <sub>2</sub> O	2.38	+H <sub>2</sub> O	0.46
H <sub>2</sub> O+	2.26	1249		100.00		100.13
	100.13					

<sup>1</sup> Analyst: Lucile N. Tarrant.

→andalusite. The relations shown in the thin section are not definitive, but by analogy with the occurrence at Goat Mountain the suggested relation is strengthened. Figure 3 shows these two types of sillimanite, two types of andalusite, and kyanite side by side in the thin section. Probably the brown sillimanite (sill I) is earlier and was in part altered to kyanite (ky), which in turn was altered to strained andalusite (and I). Many of the small fragments when immersed in heavy liquids showed parallel intergrowths of thin lamellae of kyanite and sillimanite, suggesting a simultaneous crystallization. Part of the colorless needles of sillimanite were probably derived directly at the expense of brown sillimanite. The place of the individual large andalusite crystals (and II) in the sequence of recrystallization is not clear except that they are earlier than the late sillimanite needles.

#### Other occurrences

Further field studies have revealed that layers of a similar kyanite-andalusite-sillimanite-cordierite gneiss are well exposed in the deep gorge of the Little North Fork of the Clearwater River north of Smith Ridge (1218, Fig. 2). These layers are on the top of the anorthosite, as is also a

layer of a coarse kyanite-andalusite-sillimanite-cordierite schist on the south slope of Smith Ridge along the North Fork of the Clearwater River (1302, Fig. 2).

Boulders and small outcrops of coarse bluish-gray kyanite-andalusite-cordierite-biotite gneiss with some sillimanite were found along the road leading from Boehls to Goat Mountain, about a mile south of the county boundary (937, Fig. 2). An anorthosite body occurs just north of this locality and abundant loose amphibole-bearing quartzite blocks south of it. Some of these blocks contain cummingtonite, and others have diopside, hornblende, and magnesium-rich biotite as dark constituents. Epidote with plagioclase ( $An_{37}$ ) was found in some.

#### *Andalusite-kyanite schist on the North Fork of Clearwater River*

The andalusite-kyanite-sillimanite-biotite schist on the south side of the North Fork of Clearwater River about 6 miles east of Larson Cabin (595, Fig. 2) is a dark-gray biotite schist with white andalusite nodules and white quartz blebs (Pl. 2a). The andalusite nodules range from 1 mm. to 4 cm. in diameter. The quartz blebs are usually larger and elongated parallel to the schistosity. Microscopic study shows that in addition to andalusite this schist contains abundant kyanite and some sillimanite (Pl. 2b). The other minerals are quartz, plagioclase ( $An_{46}$ ), biotite, muscovite, tourmaline, and cordierite.

#### Minerals in the schist

Most of the andalusite nodules are surrounded by a narrow rim of quartz and many of them include sericite. The indices of refraction of andalusite are  $\alpha = 1.631 \pm 0.001$ ,  $\beta = 1.638 \pm 0.001$ ,  $\gamma = 1.643 \pm 0.001$ .

Kyanite crystals in this rock (595, Fig. 2) are rather small, but in the nearby anorthositized<sup>1</sup> schist (596, 598, Fig. 2) they grow as large holoblasts including quartz or are surrounded by andalusite (pl. 3a and b). Sillimanite in the schist (595) occurs as small needles either next to the kyanite or andalusite or among the other minerals.

Biotite is light greenish brown with bright interference colors. It has  $\alpha = 1.568 \pm 0.001$  and  $\gamma$  and  $\beta = 1.610 \pm 0.001$ . Sericite is scarce and is usually included in biotite. Quartz and plagioclase ( $An_{46}$ ) are the light-colored constituents; they occur as small lentils and as scattered grains among the other minerals. Tourmaline in small prisms and a little magnetite are the accessories.

#### Relation of the aluminum silicates in the schist

All three modifications of  $Al_2SiO_5$  occur as individual grains in the schist, and there are no signs of alterations or disequilibrium except for

<sup>1</sup> Term according to Barth, 1952, pp. 229, 363.



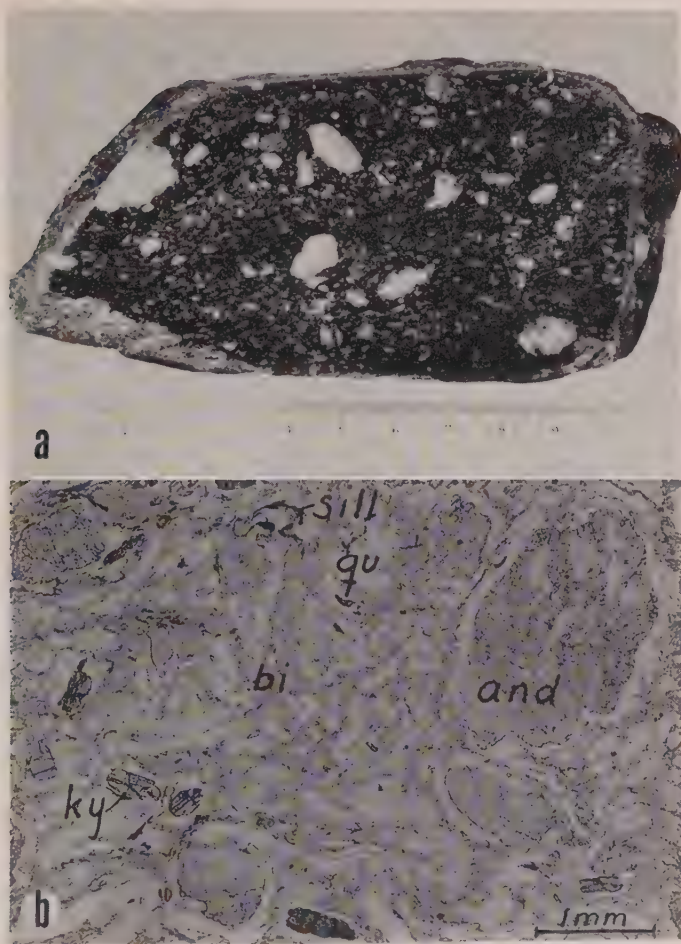


PLATE 2

- a.* Polished hand specimen of a kyanite-andalusite-sillimanite schist from North Fork of Clearwater River, 1 mile west of the mouth of Salmon Creek (595), Clearwater County, Idaho. The large rounded white areas are andalusite; small white minerals are kyanite. Abundant biotite makes the rock dark.
- b.* Photomicrograph of the same rock (595). ky=kyanite, and=andalusite, sill=sillimanite, bi=biotite, qu=quartz, +Nicols.

an unusual texture of the andalusite. The rounded nodules of andalusite are built of small elongated grains, part of which are arranged in a radiate manner. The small grains show strain shadows under the microscope. This texture is typical of the major part of the andalusite in this area, and it is clearly shown under crossed nicols in Plate 4*b*.

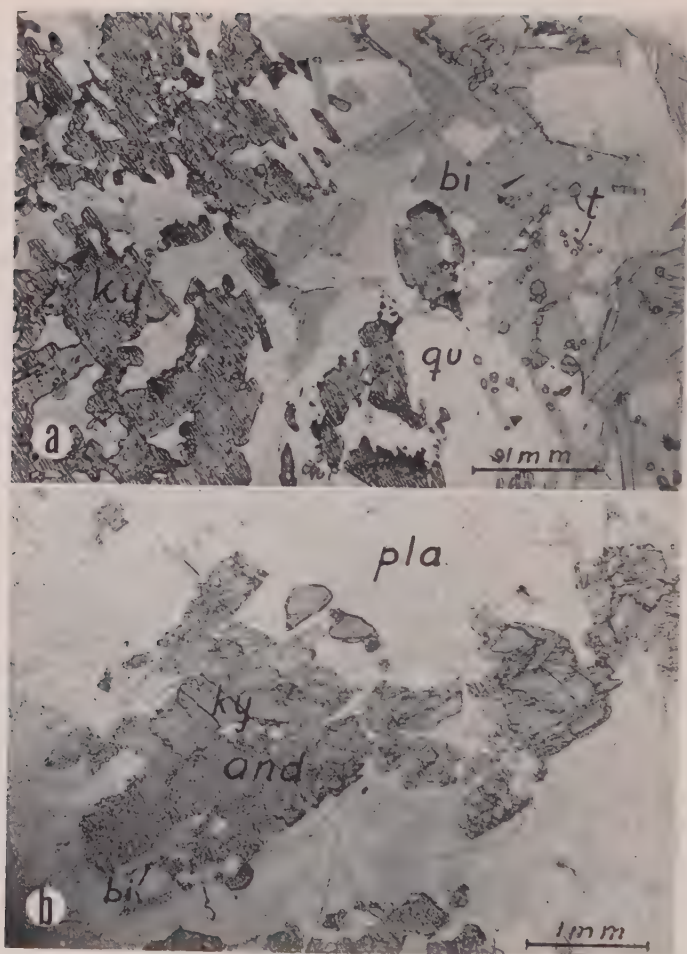


PLATE 3

- a. Kyanite holoblasts in a schist layer in anorthosite from 596, North Fork of Clearwater River, 3 miles west of mouth of Salmon Creek, Boehls Butte quadrangle. ky=kyanite, bi=biotite, t=tourmaline, qu=quartz, —Nicols.
- b. Kyanite surrounded by andalusite in the anorthosite at 598, on North Fork of Clearwater River, 3 miles west of the mouth of Salmon Creek, Boehls Butte quadrangle. —Nicols.

### Continuation of the schist layer

The westward extension of this schist parallel to the strike is metasomatically transformed to kyanite- and andalusite-bearing anorthosite, and the place of the eastward extension is occupied by an intrusive quartz monzonite which in places contains dark spots of cordierite. With two





PLATE 4

- a. Photograph of an outcrop of a coarse kyanite andalusite-sillimanite schist, 971 from Goat Mountain, Boehls Butte quadrangle. Large kyanite crystals stand out on the rock surface.
- b. Photomicrograph of a cross section of a large kyanite crystal from the rock shown in a. Main part of the kyanite (ky) has inverted to andalusite (and), which grows perpendicular to the cleavage of the kyanite and shows strain shadows. Crossed Nicols.

exceptions only sillimanite and garnet were found in the mica schists south of this location.



FIG. 3. A camera lucida drawing of the kyanite-andalusite-sillimanite-cordierite gneiss 912 from Smith Ridge, Clearwater County, Idaho. ky=kyanite, and I=early andalusite, and II=late andalusite, sill I=brown sillimanite, sill II=colorless sillimanite needles, cor=cordierite, bi=biotite, ser=sericite, qu=quartz, zr=zircon.

### *Kyanite-andalusite schist in the Goat Mountain area*

The schist surrounding the anorthosite in the Goat Mountain area is exceptionally coarse grained, containing large kyanite and andalusite crystals. Sillimanite is usually present but only in small amounts. The occurrence of cordierite in some layers and staurolite in others indicates a variation in the amount of iron and magnesium.

The schist south of Goat Mountain Lookout contains many huge kyanite crystals embedded in coarse biotite-plagioclase schist. Plate 4a shows a photograph of an outcrop of this schist. Some of the kyanite crystals are 12 inches long. The other constituents of this coarse kyanite-andalusite schist are biotite, quartz, cordierite, plagioclase, sillimanite, white mica, and several small grains of corundum.



## Minerals in the schist at Goat Mountain

The indices of refraction of the kyanite and andalusite are identical with those of the same minerals in the rock from locality 912 (Table 1). In addition the identity of these minerals was confirmed by *x*-ray powder patterns made by F. A. Hildebrand. Biotite is greenish and occurs in large flakes that show  $\gamma = 1.610 \pm 0.001$  and  $\gamma - \alpha = 0.045 \pm 0.001$ . The greenish color and abundant iron oxide along the cleavage planes and borders suggest that alteration has started. The white mica occurs in groups of small soft flakes that have  $\beta = 1.594 \pm 0.001$  and  $\gamma = 1.600 \pm 0.001$ . The *x*-ray determination made by F. A. Hildebrand shows that this mica is muscovite. In this rock cordierite occurs as elongated grains in biotite (Pl. 5a) and is altered to pinite along the borders and cracks. The composition of the plagioclase ranges from An<sub>10</sub> to An<sub>17</sub>, and a few crystals show weak zoning. Part of the plagioclase was probably introduced metasomatically during the anorthositization.

## Chemical composition of kyanite and andalusite

Kyanite and andalusite were separated from a single large crystal (containing both of these minerals) and analyzed chemically. The results in Table 4 show that the chemical compositions of these minerals are prac-

TABLE 4. CHEMICAL ANALYSES<sup>1</sup> OF KYANITE AND ANDALUSITE FROM A LARGE CRYSTAL FROM GOAT MOUNTAIN, BOEHLS BUTTE QUADRANGLE

	Kyanite		Andalusite	
	Weight per cent	Mol.	Weight per cent	Mol.
SiO <sub>2</sub>	36.76	6096	36.74	6093
TiO <sub>2</sub>	0.01	1	0.01	1
Al <sub>2</sub> O <sub>3</sub>	62.74	6150	62.70	6149
Fe <sub>2</sub> O <sub>3</sub>	0.32	20	0.36	23
FeO	0.01	1	0.05	7
MnO	0.00		0.00	
MgO	0.04	10	0.03	7
CaO	0.00		0.02	4
Na <sub>2</sub> O	0.00		0.00	
K <sub>2</sub> O	0.12	13	0.07	7
P <sub>2</sub> O <sub>5</sub>	0.00		0.00	
H <sub>2</sub> O—	0.01	6	0.01	6
H <sub>2</sub> O+	0.14	78	0.15	83
	100.15		100.14	

<sup>1</sup> Lucile N. Tarrant, *analyst*.

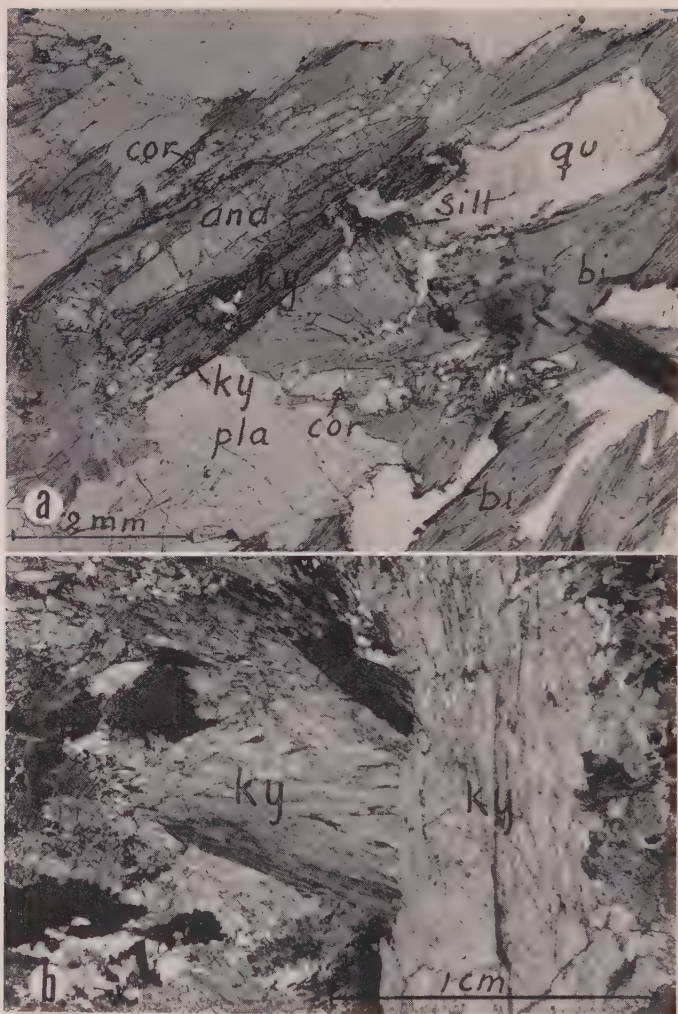


PLATE 5

- a. Photomicrograph of a kyanite andalusite-sillimanite schist from a locality half a mile east of 971 along the strike. This specimen, 967, is much finer grained than 971. ky = kyanite, and = andalusite, sill = sillimanite, cor = cordierite, bi = biotite, pla = plagioclase, qu = quartz. Note pinitization in cordierite (dark).
- b. Radiating needles of kyanite in kyanite-andalusite rock 905 from Goat Mountain Bohls Butte quadrangle. Crossed Nicols.

tically identical. Both are very pure aluminum silicates except for a small amount of  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{H}_2\text{O}$  in each. The amount of the other oxides is negligible and within the limits of the analytical error. There is no no-



table difference in the amounts of minor elements in the kyanite and andalusite (Table 5); small amounts of Ba, Cr, Cu, Ga, and V occur in each.

TABLE 5. SPECTROCHEMICAL ANALYSIS<sup>1</sup> FOR MINOR ELEMENTS  
IN KYANITE AND ANDALUSITE

	<i>Kyanite</i> Smith Ridge (Table 2)	<i>Kyanite</i> <sup>1</sup> Goat Mountain (Table 4)	<i>Andalusite</i> Goat Mountain (Table 4)
Ba	0.003	0.007	0.002
Cr	0.0006	0.0001	0.0008
Cu	0.0008	0.0008	0.0004
Ga	0.001	0.0008	0.0008
V	0.001	0.001	0.001

Not found: Ag, As, B, Be, Bi, Cd, Co, Ge, In, La, Mo, Nb, Ni, Pb, Pt, Sb, Sc, Sn, Sr, Ta, Th, Tl, U, W, Y, Yb, Zn, Zr.

#### Relation of the aluminum silicates in the schist at Goat Mountain

The large kyanite crystals show the platy habit typical of this mineral. The major part of the andalusite occurs in similar platy crystals, suggesting that they are pseudomorphs after kyanite. Many crystals consist in part of white dull massive andalusite, whereas the other part is bluish clear kyanite with a good cleavage.

The same relations are clearly shown under the microscope. Plate 4b shows a cross section of a large kyanite crystal that is altered almost completely to andalusite. The andalusite crystals grow perpendicular to the cleavage and to the walls of the cracks in the kyanite, and they show undulatory extinction and a fan-shaped texture. In some individual units half consists of kyanite and the other half of andalusite, or remnants of kyanite occur as thin lamellae in the andalusite. Sillimanite needles grow around the kyanite crystals or are included in quartz and plagioclase.

#### "Sillimanite" gneiss

Another interesting rock in the Goat Mountain area is a coarse "sillimanite" gneiss that crops out on the south slope of the Black Dome Peak (995, Fig. 2). About 50 per cent of this rock consists of large radiating light-brownish fibrous nodules, which megascopically look like sillimanite but whose indices of refraction are  $\alpha = 1.713 \pm 0.001$ ,  $\beta = 1.722 \pm 0.001$ ,  $\gamma = 1.728 \pm 0.001$ , that is, those of kyanite. Plate 5b shows a photomicrograph of such kyanite. This kyanite is probably a pseudomorph after

<sup>1</sup> Paul R. Barnett, *analyst*.

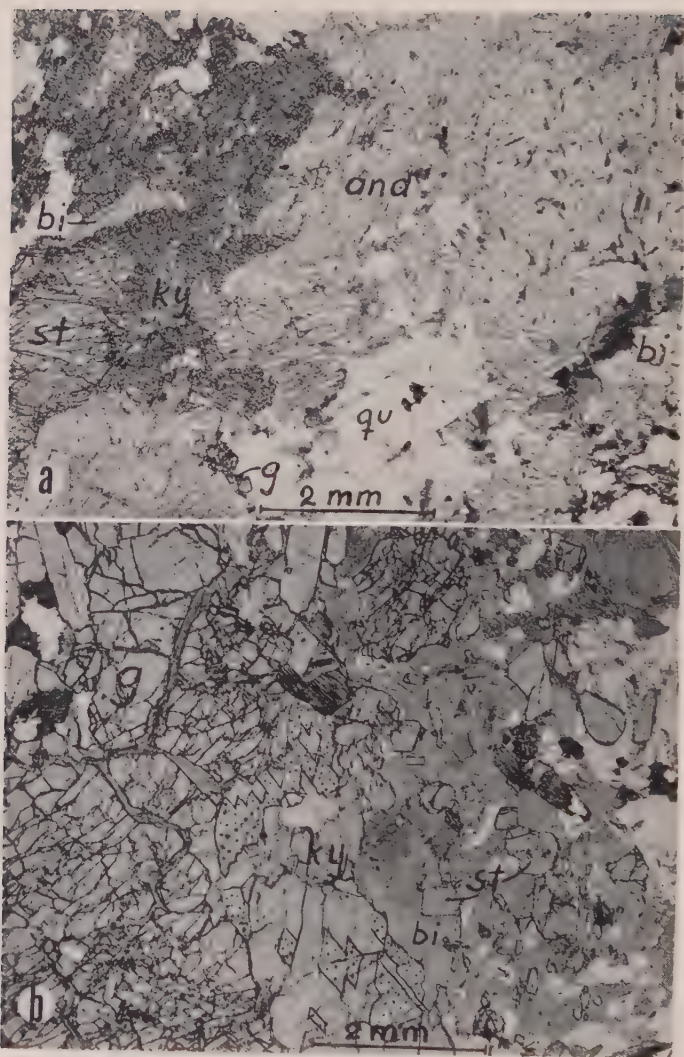


PLATE 6

- a. Photomicrograph of a staurolite kyanite-andalusite schist from a locality just north of 995 at Black Dome Peak, Bochs Butte quadrangle. st=staurolite, ky=kyanite, and=andalusite, g=garnet, bi=biotite.
- b. Photomicrograph of a kyanite-garnet schist from a locality just north of 971 at Goat Mountain. ky=kyanite, g=garnet, st=staurolite, bi=biotite. Large kyanite crystals are twinned. Twinning lamellae are shown by dotted areas. Staurolite is included in biotite and occurs as small euhedral crystals.



sillimanite. Thin-section study shows that the other constituents in this rock are andalusite, quartz, and very light brown biotite, much like the biotite in the rock 912 (Table 2). Andalusite occurs in individual large grains and also as groups of small strained grains. The individual large grains contain small quartz inclusions and are not strained. The groups of small strained andalusite grains are similar to those which were interpreted as an alteration product after kyanite in the coarse kyanite-andalusite schist (971, Pl. 4). There are also long prisms with a weak undulating extinction and with some small quartz inclusions. It is possible that the individual unstrained andalusite grains were recrystallized at the expense of the strained crystals during the continued thermal metamorphism. Thus, the sequence of crystallization here might be as follows: sillimanite→kyanite→strained andalusite→clear andalusite. Some of the needlelike minerals are andalusite, and it is possible that part of the sillimanite was transformed directly to andalusite.

#### Staurolite-bearing schist

The rocks described above are rich in magnesium, containing cordierite and magnesian biotite. Above this magnesium-rich zone of the Goat Mountain area are iron-rich beds that contain abundant garnet, staurolite, reddish-brown or green biotite, and ilmenite. Brown grains of rutile and small round crystals of zircon occur as accessories. Also these layers are rich in kyanite and andalusite (Pl. 6*a* and 6*b*), but no sillimanite was found in thin sections made of specimens from Black Dome Peak and from an area just north of locality 971.

The relation between staurolite, kyanite, and andalusite at Black Dome Peak (Pl. 6*a*) suggests that staurolite was crystallized early and was partly altered to kyanite, which in turn was transformed to andalusite. With the kyanite and andalusite small flakes of biotite and ilmenite-magnetite occur; they contain the iron that was released from the staurolite. Biotite and garnet show incipient alteration to chlorite.

In the garnet-kyanite-andalusite schist just north of the coarse kyanite-andalusite schist (971, Fig. 2) small euhedral staurolite crystals are included in biotite, and kyanite occurs in large anhedral grains that show twinning (Pl. 6*b*). Andalusite appears in nodules of small strained grains. Garnet crystals abound, some of which measure 2 inches in diameter. In the Monumental Buttes area (1152, fig. 2) schist similar to the rock 971 is exposed between a coarse kyanite-andalusite schist and the quartzite in the middle of the Prichard formation. This schist is obviously a continuation of the iron-rich layer at Goat Mountain.

*Sillimanite-kyanite-andalusite schist west of Goat Mountain*

Layers rich in sillimanite are common in schist southwest of the anorthosite on Goat Mountain (953, 954, 1368, Fig. 2). Some of these layers contain abundant kyanite and others are rich in andalusite. Brown biotite, staurolite, and garnet are the common dark constituents. Most



FIG. 4. A camera lucida drawing of the sillimanite-andalusite schist 1368 from an area 2 miles southeast of Orphan Point on the southwest side of the anorthosite on Goat Mountain, showing replacement of biotite by sillimanite and sillimanite by andalusite. and=andalusite, sill I=brown sillimanite, sill II=colorless sillimanite needles, bi=biotite, qu=quartz, pla=plagioclase.

of this schist is strongly feldspathized, showing a complete transition from schist to anorthosite.

Microscopic study shows that biotite in this schist is partly altered to sillimanite. Most of the biotite is darker brown than in any of the schists described above. But those flakes that seem to be altering to sillimanite



are pale in color. The alteration of biotite to sillimanite is clearly seen under the microscope in the schist 1368 and in specimens 954 and 1404 of feldspathized schist. First a nodule of brown fibrous sillimanite is formed. During the advancing crystallization larger colorless needles surround the brownish nodule, which then shows irregular parting. In the specimen 954 a part of the sillimanite in the nodule is crystallized as small prisms of sillimanite, the other part as larger crystal of kyanite which is then surrounded by sillimanite or andalusite. Andalusite also occurs as nodules built of strained small crystals and containing rounded quartz inclusions. In the specimen 1368 a part of the brown sillimanite nodules is inverted to andalusite, which shows a relic parting similar to that in the sillimanite (Fig. 4). There are also andalusite grains without such parting. Many of these andalusite grains include remnants of staurolite.

In the specimen 1404 sillimanite, kyanite, and andalusite occur in aggregates next to each other. Sillimanite aggregates consist of light brownish to colorless needles which show fan-shaped or parallel arrangement and grade over to andalusite. Some kyanite crystals include sillimanite and are surrounded by andalusite suggesting that reactions  $\text{sillimanite} \rightarrow \text{kyanite} \rightarrow \text{andalusite}$  took place. The reactions  $\text{biotite} \rightarrow \text{sillimanite}$  and  $\text{staurolite} \rightarrow \text{andalusite}$  indicate increase of aluminum and decrease of iron and potassium in this schist. The inversion  $\text{sillimanite} \rightarrow \text{andalusite}$  probably took place during the same phase as the alteration of kyanite to andalusite in the Goat Mountain area.

Reactions similar to those in the schist were observed also in the anorthosite along its border zones. As a rule the border zones of the anorthosite contain abundant aluminum silicates, garnet, and biotite. Remnants of staurolite are common in the Goat Mountain area (e.g. loc. 1353) and cordierite occurs near Smith Ridge (loc. 1412).

#### SUMMARY OF THE ALTERATIONS INVOLVING THE ALUMINUM SILICATES

The following sequence of alterations were observed in thin sections:

- (1) Biotite  $\rightarrow$  sillimanite in six specimens (953, 954, 1353, 1368, 1404, 1412).
- (2) Staurolite  $\rightarrow$  kyanite in one specimen (997).
- (3) Staurolite  $\rightarrow$  andalusite in two specimens (1353, 1368).
- (4) Sillimanite  $\rightarrow$  kyanite in six specimens (912, 953, 954, 995, 1404, 1412).
- (5) Sillimanite  $\rightarrow$  andalusite in two specimens (1368, 1404).
- (6) Kyanite  $\rightarrow$  andalusite in ten specimens (596, 598, 953, 971, 995, 997, 1011, 1017, 1152, 1404).
- (7) Kyanite  $\rightarrow$  sillimanite in two specimens (912, 1218).
- (8) Andalusite  $\rightarrow$  sillimanite in two specimens (912, 1218).

The brownish fibrous sillimanite is derived, as an alteration product, from biotite, and this same sillimanite was found to be altering further

to kyanite, andalusite, or colorless sillimanite. When sillimanite is formed at the expense of andalusite or kyanite (912), it is a needlelike colorless variety. Andalusite also exhibits two varieties: (1) normal-looking individual grains, and (2) clusters or nodules of small strained grains. The latter variety is an alteration product after kyanite.

In summary, it can be said that in the northern part of the Boehls Butte quadrangle the reactions: sillimanite→kyanite→andalusite are common, whereas in the southern part of the quadrangle the reactions kyanite→andalusite→sillimanite and kyanite→sillimanite can be seen. Thus, part of the reactions were reversed in the southern part during a later phase, probably during the emplacement of quartz monzonites. No transformation andalusite→kyanite was seen in the thin sections studied.

#### RELATION OF THE INVERSIONS OF THE ALUMINUM SILICATES TO THE SEQUENCE OF GEOLOGIC EVENTS

The sequence of alterations listed above show that, first, either sillimanite or sillimanite and kyanite were crystallized. According to the literature kyanite is usually found to crystallize at low temperatures, high pressures, and under stress; sillimanite at high temperature. Their contemporaneous crystallization suggests a fairly high pressure and temperatures at which both would be stable. Both these minerals were crystallized during the folding and regional metamorphism, as were staurolite, cordierite, and biotite, with which they are associated.

During a study of metasomatism in a wider region northwest of the Idaho batholith, it was found that there are several phases of igneous intrusion, metamorphism, and metasomatism. Folding and regional metamorphism were found to be earlier than the metasomatism that formed the anorthosite.

Three major phases of intrusion were distinguished on the basis of structural relations: (1) During the earliest phase small bodies of gabbro and quartz diorite were emplaced. These bodies reveal generally concordant contacts, and the mineral alignment is much like that in the folded country rock. (2) The quartz dioritic border zone of the Idaho batholith cuts the folded country rock in many places discordantly and is thus post-folding; minerals in the quartz diorite show less alignment than those in the small satellitic bodies. Late metasomatic development of andesine and hornblende in the schist and formation of anorthosite bodies are probably connected with this phase of intrusion. (3) Quartz monzonite and silicic tonalite were emplaced later than quartz diorite; they cut the rocks that were metasomatized during the emplacement of the quartz diorite. Thus, both temperature and stresses were fluctuating



during the development of the mineral associations. Probably the fluctuation of stresses was favorably timed with that of the temperature to cause the inversions described above.

Crystallization may have proceeded as follows: raising of temperature during the regional metamorphism gave rise to the crystallization of kyanite at the expense of staurolite and crystallization of sillimanite at the expense of biotite. Probably the maximum temperature of regional metamorphism was attained and the temperature had started to fall while the stresses were still operating, causing a rare transformation of sillimanite to kyanite.

The inversion of kyanite to andalusite is later, belonging possibly to the period of the iron-magnesium metasomatism (Table 6), which is post-folding in this area.

In the anorthosite and near its contact, remnants of andalusite are included in metasomatic bytownite, showing that the andalusite crystallized before the anorthitic plagioclase was formed. In an area 20 to 30 miles southwest of Boehls, Fe and Mg were introduced before Ca and Na. In Boehls Butte quadrangle, layers and lenticles of garnet amphibolite, which are common in the schist around the anorthosite bodies and earlier than them, represent basic rocks formed during the iron-magnesium metasomatism. It is possible that the kyanite was altered in part to andalusite under the influence of the metasomatizing solutions during the formation of the garnet amphibolite. Later calcium, which was introduced shortly after iron and magnesium, reacted with this andalusite and formed bytownite.

Colorless sillimanite needles in the southern part of the Boehls Butte quadrangle are later than the andalusite. The transformation of kyanite and andalusite to sillimanite is probably due to a thermal effect caused by the emplacement of nearby igneous rocks belonging to the quartz monzonite series. It is noteworthy that only sillimanite occurs in the zone next to the batholith (south of the Boehls Butte quadrangle). It seems that sillimanite had already crystallized in this zone during the emplacement of the quartz dioritic border zone of the batholith and was in part altered to sericite during the emplacement of quartz monzonites. This transformation requires an addition of potash and occurs only locally.

The relation of these transformations to the sequence of the geologic events is summarized in Table 6.

Inversion of sillimanite to andalusite was seen in two thin sections from a schist west of Goat Mountain. This inversion was suspected in two specimens from the Goat Mountain area, but neither of these was convincing, as it was impossible to determine in thin section whether

kyanite had appeared as a metastable form during the transformation. Tilley (1935) described the alteration of andalusite to kyanite in the Carn Chuinneag granite from Ross-shire, Scotland, where regional metamorphism was superimposed on normal thermal metamorphism; and Bosworth (1910) described such alteration around the Ross of Mull granite in Scotland; he also reported parallel growths of andalusite and sillimanite in cordierite-bearing rocks from the same area. Two of these minerals are commonly found together, and it is usually believed that these associations represent arrested transformations. Miyashiro (1949) has discussed stability relations of kyanite, andalusite, and sillimanite, suggesting that each of these minerals has its own stability field and that there is a triple point where all three are stable. However, his diagram

TABLE 6. RELATION OF THE TRANSFORMATION OF THE ALUMINUM SILICATES TO THE SEQUENCE OF GEOLOGIC EVENTS IN BOEHLS BUTTE QUADRANGLE

Geologic events	Transformations
1. Intrusion of gabbros and diorites; folding and regional metamorphism accompanied by metasomatism 1, that is, introduction of Fe, Mg, Al, Ca.	Biotite→sillimanite→kyanite Staurolite→kyanite
2. Emplacement of quartz dioritic border zone of the batholith accompanied by metasomatism 2. (a) Introduction of Fe and Mg (b) Introduction of Ca (anorthositization)	(a) Staurolite→andalusite Sillimanite→andalusite Kyanite→andalusite (b) Andalusite→bytownite (in part)
3. Emplacement of quartz monzonites accompanied by (a) Thermal metamorphism (b) Metasomatism 3 (introduction of alkalis)	(a) Kyanite→sillimanite Andalusite→sillimanite (b) Sillimanite→muscovite (locally)

fails to give definite figures for the temperature and pressure of the triple point. Turner and Verhoogen (1951, p. 412) have suggested that the sillimanite is a stable form and that andalusite would appear because the reaction producing andalusite is faster. Wilson (1929) suggested that in a dumortierite occurrence in Yuma County, Arizona, kyanite, andalusite, and sillimanite are metasomatic, the kyanite and andalusite being earlier than the sillimanite.

In the light of the present study the sillimanite could be inverted to kyanite by stresses operating at a moderate temperature. But this kyanite would be stable only under stress and would invert to andalusite under the influence of metasomatizing solutions when the stress is released, or revert to sillimanite if the temperature is raised (Fig. 5).

Many occurrences of kyanite in quartz veins show that kyanite can be formed at low temperatures without stress. Verhoogen (1951, p. 258) has shown that during the formation of minerals hydrostatic pressure can substitute for stress. Thus, kyanite would crystallize also under hydrostatic pressure at low temperature, whereas andalusite would be formed if the pressure were lower and/or the temperature somewhat higher.

It is interesting to note that cordierite, which is considered an anti-stress mineral, is a common constituent in the kyanite schists. In some specimens from the Goat Mountain area, it was included in biotite, thus appearing as an unstable relic; but in the Smith Ridge rock it is fresh

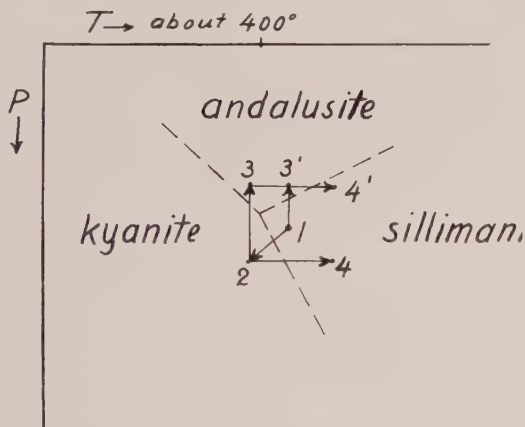


FIG. 5. Diagram showing the possible fields of stability and the inversions of the three aluminum silicates. Stresses or raising of pressure during a falling temperature would cause an inversion sillimanite→kyanite (1→2). During the metasomatism in static conditions kyanite and sillimanite were converted to andalusite (2→3, and 1→3'). Raising of temperature caused inversions andalusite→sillimanite (3 and 3'→4') and kyanite→sillimanite (2→4).

and shows no signs of incompatibility with the kyanite. This suggests that the stability fields of kyanite and cordierite overlap and that a somewhat higher pressure or a stronger stress than that needed to form kyanite is required to make the cordierite unstable.

#### TEMPERATURE AND PRESSURE OF THE INVERSIONS SILLIMANITE⇌KYANITE⇌ANDALUSITE

The mineral assemblages are:

- (1) Kyanite-andalusite-sillimanite-cordierite-biotite-muscovite-corundum.
- (2) Kyanite-andalusite-sillimanite-staurolite-garnet-biotite-muscovite.
- (3) Hornblende-diopside-epidote-andesine (An<sub>36</sub>).

These assemblages suggest that the rocks in Boehls Butte quadrangle



were metamorphosed in the border between the kyanite schist facies (Barth, 1952, p. 340) and the amphibolite facies, the temperature being thus around 400° C. In the contact zone between anorthosite on Goat Mountain and garnet amphibolite, abundant epidote occurs with plagioclase ( $An_{36}$ ). According to Ramberg (1949) and Barth (1952), the temperature at which this plagioclase would crystallize with epidote is close to 400° C. It seems, therefore, that the temperature of the inversion sillimanite→kyanite→andalusite, a relation common in the Goat Mountain area, was close to 400°.

In the southern part of the area, where only sillimanite occurs, the temperature was probably between 400° and 500°, corresponding to the temperatures in the amphibolite facies.

The basification and anorthositization (Table 6) in the area south of Boehls Butte quadrangle probably took place at fairly shallow depths. It is only natural that the same conditions prevailed also in Boehls Butte quadrangle and that the inversion kyanite→andalusite, which is thought to be connected with this second period of metasomatism, therefore took place at moderate or low pressure.

#### CONCLUSION

The recorded transformations between kyanite, andalusite, and sillimanite are ascribed to the fluctuation of temperature and stresses (pressure) during a complex thermal metamorphism superimposed on a regional metamorphism in the border zone of the composite Idaho batholith. All the inversions except andalusite→kyanite were observed in the thin sections. This transformation in several areas where regional metamorphism has followed thermal metamorphism has been described in the literature. It seems, therefore, that at certain temperatures both andalusite and sillimanite can be inverted to kyanite under stress. On the other hand, andalusite and kyanite alter to sillimanite at higher temperatures, and kyanite readily to andalusite under the influence of metasomatizing solutions if stresses are released. Thus, each of the three modifications of  $Al_2SiO_5$  may be transformed to the others under certain physico-chemical conditions. It is possible that each of these aluminum silicates has its own stability field and that these stability fields have a common point or overlap to some extent because two of the aluminum silicates, or in rare cases all three, may exist simultaneously. Kyanite is usually found in rocks metamorphosed at low temperatures under stress or high pressure, andalusite at moderate temperatures and low pressures under static conditions, and sillimanite at the highest temperatures in regionally metamorphosed areas. The occurrence of all three modifications together in the schist in Boehls Butte quadrangle suggests that

the temperature and pressure during the complex regional and thermal metamorphism there fluctuated around the field where all modifications may exist in equilibrium. The association of epidote and plagioclase ( $An_{36}$ ) suggests that the temperature field is around  $400^{\circ}$  C.

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# ON THE GENESIS OF RESIDUAL KAOLINS\*

L. B. SAND

## ABSTRACT

A study of weathered feldspathic rocks in the Southern Appalachian region revealed that hydrated halloysite forms by the weathering of all types of feldspar where environmental conditions are favorable, as in the Spruce Pine district of western North Carolina. Further south and north of this district in the Blue Ridge province and east into the Piedmont province, the potash feldspar increasingly alters to vermicular kaolinite through the intermediate stage of secondary mica, until all feldspars alter to kaolinite and only small amounts of hydrated halloysite are formed. Hydrated halloysite, and not its dehydrated product, is found in all deposits, which indicates environmental conditions have not changed appreciably since Tertiary time. Hydrated halloysite and kaolinite are formed independently; there was no evidence of transitions between the varieties. Primary mica and secondary mica formed by weathering of feldspar always alter to vermicular kaolinite.

Quantitative mineralogical analyses were made on samples from most of the deposits by the thin-section point counter technique and by x-ray diffraction and glycol-differential thermal analyses of size fractions.

## INTRODUCTION

Kaolinite and hydrated halloysite occur as mixtures in residual clay deposits. Halloysite occurs as a dehydration product in some deposits in exposed mine faces. The reason for the occurrence of mixtures of kaolinite and hydrated halloysite had not been established clearly. For this reason a detailed mineralogical study of the residual kaolins of the Southern Appalachian region was undertaken in an attempt to ascertain the conditions giving rise to these compositionally similar clay minerals during the processes of weathering. In both the Blue Ridge and Piedmont physiographic provinces, good deposits for sampling are afforded by the strip mines producing mica and kaolin derived from the weathering of granites and pegmatites. An areal map showing distribution of the areas sampled is shown in Fig. 1. The deposits sampled in western North Carolina are described by Hunter and Hash (1949).

## LITERATURE REVIEW

Composition of the pegmatites over this entire region is remarkably uniform according to Parker (1949) with the typical rock consisting essentially of plagioclase, perthitic microcline, quartz and muscovite. The pegmatites and granites are weathered to depths up to one hundred feet

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depending on the topographic location. Deeply weathered deposits are located on river terraces; it is in these deposits that transitions from completely altered feldspar grading into parent material are exposed by mining operations.

According to Parker (1946) the most extensive period of kaolinization in the Spruce Pine district of western North Carolina occurred during the period in which the terraces were formed. The altitude of these terraces led Bridges (1949) to suggest that they could be considered as intermontane extensions of the Harrisburg peneplane of early Tertiary age. Bridges states that rocks in the Blue Ridge region were weathered deeply during the interval beginning with the uplift of the Schooley or Kitta-

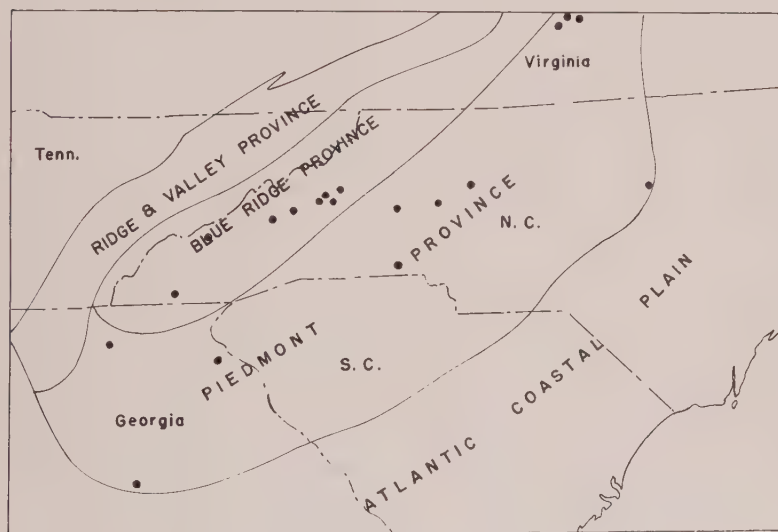


FIG. 1. Areal map showing locations of deposits sampled.

tinny peneplane and throughout the period in which the Harrisburg peneplane was being formed. Hunter (1940) and others observed that the depth of alteration coincides with the lowest level at which water freely circulates and the clay deposits occupy such a position relative to the river levels.

Ross and Kerr (1930, 1934), in their classic contributions concerning minerals of the kaolin group, state that halloysite very commonly is associated with kaolinite in some deposits, especially residual deposits derived from pegmatites. They suggest that halloysite occurring under such conditions might represent a stage in the eventual crystallization of kaolinite. Hunter and Hash (1949), conversely, suggest that in the

halloysite deposits of western North Carolina alternate wetting and drying, with the possibility of aeration, might have been influential in the conversion of kaolinite to halloysite. Hunter (1940) previously stated that optimum conditions for kaolinization obtain where the topographic features encourage drainage and where the feldspathic rock is covered by dense vegetation. Cady (1950) reports on two deposits in the Piedmont province of North Carolina; he believes halloysite is formed in regions where weathering is slow and free movement of air and water is restricted.

Early workers on these deposits (Ries, 1911; Lindgren, 1915; and Bayley, 1921) all attributed the formation of these clays to weathering. Regarding the alteration of the mica, Bayley (1925) states that near the surface the mica is altered and loses its characteristic features; he designated the decomposition product "hydromica." Selle (1876), Hickling (1908) and Galpin (1912) advocated the origin of kaolinite through the formation of mica as an intermediate product. Galpin states that it is probable that secondary muscovite, representing the first stage of the weathering of feldspars, is converted directly into kaolinite. Regarding the North Carolina deposits, Ross and Kerr (1930) call the intermediate product a muscovite-like kaolin mineral. They state that crystals form vermicular aggregates like those of kaolinite in the same deposit and that many of these groups are partially altered to kaolinite. Denison, Fry and Dile (1929) studied the alteration of mica in soil profiles and concluded from chemical and optical evidence that the muscovite alters to kaolinite.

In 1943, the relation between hydrated halloysite (endellite) and its dehydrated product (halloysite) was elucidated by Alexander, *et al.* The tubular morphology of halloysite was determined by Bates, *et al.* (1950).

#### METHODS OF INVESTIGATION

Analyses of dry clay samples collected in 1950 disclosed the need for keeping the clays in their original hydrated condition and for the development of quantitative techniques. Moist samples were collected in 1951 with Professor T. F. Bates of The Pennsylvania State University.

A differential thermal analysis technique was developed which identified the amount of hydrated halloysite and kaolinite in a sample (Sand and Bates, 1953). Techniques used for quantitative analysis of dry samples containing halloysite and kaolinite are described by Sand and Ormsby (1953).

To determine quantitatively the mineral content of the residual clays, two corroborative methods were used; namely, point counts of thin-sections and analyses of size fractions by x-ray diffraction and glycol-

differential thermal analysis. The point counter method, as modified by Chayes (1949) was applicable since, in most of the samples studied, the kaolinite occurred as vermicular aggregates easily distinguished from halloysite. Where the mica was in an intermediate stage of decomposition, it was difficult at times to differentiate between the interleaved kaolinite and parent mica. Size fractionation was employed to make mineral separations on the basis of particle size. Quartz and feldspar generally concentrated in the coarsest fractions, mica and kaolinite in intermediate fractions and hydrated halloysite in the finest fractions. The samples were milled with a rubber pestle, the suspension brought to  $pH=10$  by addition of ammonium hydroxide and blended for five minutes. This treatment did not disaggregate the hydrated halloysite completely, but did prevent the disaggregation of the relatively coarse "books" of kaolinite and mica. Wet-sieve separations were made through 60 and 200 mesh screens and gravity separations were made through the 8 micron size fraction. For separating finer fractions, centrifuge methods were used. Size frequency distributions were obtained simultaneously. Each size fraction was analyzed by x-ray diffraction, differential thermal and petrographic techniques to obtain quantitative mineral constitution. The Norelco x-ray spectrometer was used; peak intensities were used to estimate percentages of minerals present. The moist sample first was analyzed and then dried at  $100^{\circ}\text{C}$ . to resolve the hydrated halloysite and mica basal reflections which mutually interfere.

In studying deposits of halloysite, it is advantageous to keep the samples moist for analysis. Allowing samples to become even partially dehydrated makes quantitative analysis difficult except for petrographic and electron microscope techniques. Estimates of halloysite content on the basis of electron micrographs is hazardous if the kaolinite is present as vermicular aggregates in a coarse size range. Special preparation, as by homogenization, offers some possible quantitative use for the electron microscope on such samples. In those samples where the vermicular habit of kaolinite is not well-developed, the thin-section method for quantitative determination of kaolinite versus halloysite is useless. Analysis of the moist sample by the *glycol-DTA* method is preferred in such samples. If either the kaolinite or hydrated halloysite content is low, size fractionations should be made and the fractions analyzed.

#### ANALYSIS OF SAMPLES

##### *Virginia Piedmont Province*

Samples from four deposits in this region were examined. They were found to be principally kaolinite with some hydrated halloysite present



in minor amounts. In each of the deposits, the feldspar was observed altered in part to secondary mica from which vermicular kaolinite was being derived. Samples from three of the deposits were studied in thin-section. An analysis of size fractions was made of a sample from the Nat Kidd Prospect in Roseland. This analysis is given in Table 1 to illustrate the fractions separated and analyzed. Complete analyses of other samples so analyzed are given elsewhere (Sand, 1952).

TABLE 1. MINERALOGICAL ANALYSIS OF SIZE FRACTIONS, NAT KIDD PROSPECT, ROSELAND, VIRGINIA

Size fraction (microns)	Quartz	Mica	Feldspar	Hydrated halloysite	Kaolinite	Size analysis
+250	tr.	0.2%	tr.		tr.	0.2%
74-250	0.1%	0.3			0.2%	0.6
31-74		6.1			5.9	12.0
16-31		13.2			13.4	26.6
8-16		8.6			19.0	27.6
4-8		3.1			12.3	15.4
2-4		1.3			7.2	8.5
1-2		tr.		0.1%	0.7	0.8
0.5-1		0.1		0.8	2.1	3.0
-0.5		0.2		1.4	3.7	5.3
Bulk Composition	0.1	33.1		2.3	64.5	100.0

The bulk composition of this sample correlated with the thin-section analysis of a sample from the American Rutile Mine in Roseland which contained 70% kaolinite, 29.2% mica and 0.8% quartz. This sample had dehydrated and although the amount of halloysite was not determined, only a few halloysite particles were present among kaolinite "books" and plates in the electron micrograph.

Samples taken from the Calco Ilmenite Mine at Piney River, and the Morefield Mine at Amelia Court House, were found to be similar in mineral constitution. The secondary mica in all these deposits formed in a fine-sized vermicular habit by alteration of the feldspar. The mica in turn was weathered to vermicular aggregates (about 0.02 mm. size) of kaolinite. The vermicular habit was not as pronounced as in deposits further south.

#### *North Carolina Piedmont Province*

Qualitative examination of samples from gneissoid rocks in this region showed a predominance of kaolinite over halloysite. In these samples no

vermicular habit was observed, nor was it evident that mica was an intermediate product. The small amount of halloysite present in these samples occurred as well-developed tubes up to ten microns in length.

Two moist samples from the Patterson Mica Mine were analyzed in detail. One sample consisted of a granitic material obtained thirty feet below the original surface. The kaolinite appeared in the coarsest size fractions due to interleaving with the parent mica. The bulk composition, as determined by analysis of the size fractions, is listed in Table 5. The other sample was a decomposed feldspar crystal obtained from pegmatitic material located 50 feet below the original surface. Its bulk composition is also listed in Table 5. The large variation that can obtain between clay samples in one deposit is demonstrated by these two analyses.

#### *North Carolina Blue Ridge Province (Northern Region)*

Eight deposits were studied in this region usually designated as the Spruce Pine pegmatite district. Of these, the Gusher Knob and Micaville deposits are in granitic bodies cut by pegmatite veins; the others are in pegmatites.

Hydrated halloysite predominated over kaolinite in all of these deposits. In individual samples the hydrated halloysite to kaolinite ratio varied from 30:1 to 1:1 with an average for the region of about 10:1. The feldspars, whether sodic plagioclase or microcline, weather to hydrated halloysite with plagioclase the first to decompose. This can be observed in the hand specimen of a partially altered perthite where the potash feldspar stands out in relief. Large, only slightly altered microcline crystals were found next to completely altered plagioclase. However, in this region it was found that all feldspars alter to hydrated halloysite even though the rate of weathering differs. In only one sample, from the Woody Deposit, was the potash feldspar observed altered in small part to secondary mica. The primary mica was altered to vermicular kaolinite in all samples studied.

In each of the two granitic bodies, a study was made on vertical profiles of the degradation of muscovite. In the Micaville deposit, the mica content in the finer fractions decreases upward in the soil profile. To illustrate this, the mica and feldspar contents (per cent of total composition) are excerpted from the analyses of the size fractions of sample S-21 (top), S-23 (middle) and S-27 (bottom) as shown in Table 2.

The disappearance of the muscovite in the finer fractions also was found to obtain in four vertical sections taken from a sample grid in the Gusher Knob deposit. The vertical profiles each contain three samples separated by three foot intervals. To illustrate, Table 3 lists the mica

TABLE 2. MICA AND FELDSPAR CONTENT IN A VERTICAL PROFILE,  
MICAVILLE DEPOSIT

Size fraction (microns)	Mica			Feldspar		
	Top	Middle	Bottom	Top	Middle	Bottom
+250	6.4%	6.2%	0.4%	none	none	1.1%
74-250	5.1	23.4	0.7		0.5%	3.7
31-74	1.1	3.6	10.6		0.2	15.2
16-31	1.4	3.1	2.6			2.6
8-16	0.5	2.2	2.9			0.8
4-8	0.2	0.5	1.1			0.2
2-4	0.1	0.3	0.5			
1-2		0.2	0.2			
0.5-1		0.1	0.1			
-0.5		tr.	0.3			

content (per cent of total composition) in one typical profile in the finest fraction in which mica occurs.

Because of the wide variability in total content and size distribution of muscovite between samples, inverse correlation of total mica content with total kaolinite content does not always obtain. However, the mica in the finest fractions, which is the first to alter completely, was observed to disappear upward in the profile. The grid sampling taken in the Gusher Knob Deposit was in a weathered, fairly uniform granitic body at the east end of the East pit. The samples were taken three feet apart on the vertical and ten feet apart along the horizontal. Samples 52 and 62 were the top samples in the central vertical profiles. Bulk mineral compositions, as obtained from analyses of the size fractions, are given in Table 4 to show the large sample variation.

#### *North Carolina Blue Ridge Province (Central Region)*

In Buncombe County, completely altered pegmatites, selected for detailed study, showed a general decrease in the content of hydrated

TABLE 3. MICA CONTENT IN THE FINEST FRACTION IN WHICH MICA OCCURS,  
GUSHER KNOB DEPOSIT

Sample No.	Size Fraction	Mica Content
50 top	8-16 microns	2.0%
47 middle	8-16 microns	7.5%
42 bottom	8-16 microns	10.0%



TABLE 4. BULK MINERAL COMPOSITION BY ANALYSIS OF SIZE FRACTIONS,  
GUSHER KNOB DEPOSIT

Sample No.	Quartz	Mica	Feldspar	Hydrated halloysite	Kaolinite
West Wall of Grid					
42-bottom	0.8%	17.1	0.7	66.2	15.1
47-middle	7.7	32.6	none	55.4	4.3
50-top	10.3	18.6	none	67.4	4.1
44-bottom	23.3	24.3	3.9	41.3	7.0
45-middle	16.6	14.8	0.9	55.7	12.1
52-top	15.8	8.4	none	62.5	12.3
South Wall of Grid					
54-bottom	45.0	15.2	none	29.0	11.8
59-middle	37.5	16.4	none	21.5	24.7
62-top	30.2	10.8	none	42.6	16.5
56-bottom	32.3	12.1	none	42.5	13.2
57-middle	30.8	17.7	none	31.7	19.8
64-top	38.5	11.2	none	42.3	8.0

halloysite and a corresponding increase in the amount of kaolinite over those from the Spruce Pine District. Most of the feldspar crystals, whether plagioclase or microcline, alter to hydrated halloysite. However, some of the microcline in each deposit alters to secondary mica which weathers to kaolinite. Bulk mineral compositions from the Arrowhead and Alexander deposits are given in Table 5.

#### *North Carolina Blue Ridge Province (Southern Region)*

An increase in the amount of kaolinite derived from feldspar was noted in this region. In one sample from near Hayesville, the hydrated halloysite to kaolinite ratio was 1:23. This was the only sample from this region that was so high in kaolinite content. In all other deposits in this region, including Macon, Swain, Haywood and Clay counties, the feldspar alters in part to secondary mica and the remainder to hydrated halloysite. In a perthite crystal the plagioclase alters principally to hydrated halloysite and the microcline principally to mica and eventually to kaolinite.

#### *The Georgia Piedmont*

The kaolin residual clays in this province showed a predominance of kaolinite over hydrated halloysite. The ratio of hydrated halloysite to

TABLE 5. BULK MINERAL COMPOSITIONS

Deposit	Analysis	Parent rock	Quartz	Mica	Feldspar	Hydrated halloysite	Kaolinite
<i>Va. Piedmont</i>							
Nat Kidd	S.F.	syenite	0.1	33.1	tr.	2.3	64.5
<i>N.C. Piedmont</i>							
Patterson	S.F.	granite	5.0	35.1	none	0.5	59.5
Patterson	S.F.	pegmatite	0.6	11.0	none	27.1	61.3
<i>N.C. Blue Ridge (Northern)</i>							
Gusher Knob							
Average, 12 samples	S.F.	granite	24.1	16.4	0.5	46.6	12.4
School Hill	S.F.	granite	58.2	1.9	none	35.3	4.9
Fluken Ridge	T.S.	pegmatite	22.4	0.3	0.8	73.7	2.8
Fluken Ridge	T.S.	microcline	0.4	1.3	0.3	90.8	7.2
Fluken Ridge	S.F.	microcline	0.7	7.0	4.7	74.4	13.1
Fluken Ridge	S.F.	perthite	tr.	6.4	39.7	52.2	1.7
Fluken Ridge	S.F.	perthite	4.6	2.1	75.6	16.3	1.4
17-Acre Pros.	S.F.	pegmatite	5.5	16.8	none	64.5	13.2
17-Acre Pros.	S.F.	pegmatite	8.8	18.2	none	61.8	11.1
17-Acre Pros.	T.S.	pegmatite	3.0	17.1	none	66.8	13.1
17-Acre Pros.	S.F.	pegmatite	3.4	8.3	none	75.5	12.9
17-Acre Pros.	T.S.	pegmatite	1.8	3.8	none	85.6	8.8
17-Acre Pros.	T.S.	pegmatite	none	6.3	none	84.9	8.8
Carter Ridge	T.S.	pegmatite	none	2.9	none	84.3	12.8
Micaville	S.F.	granite	4.4	14.8	none	78.0	2.7
Micaville	S.F.	granite	29.9	39.7	0.7	25.1	4.7
Micaville	S.F.	granite	5.7	19.4	21.6	43.1	10.2
<i>N.C. Blue Ridge (Central)</i>							
Arrowood	T.S.	pegmatite	none	0.6	13.9	75.1	10.4
Arrowood	S.F.	pegmatite	1.2	3.9	7.5	69.2	21.2
Alexander	T.S.	perthite	none	1.6	0.2	87.5	10.7
Alexander	T.S.	perthite	none	2.7	none	86.8	10.5
Alexander	T.S.	microcline	none	0.4	0.2	91.8	7.6
Alexander	S.F.	perthite	0.9	7.3	0.6	75.0	16.1
Alexander	S.F.	perthite	3.3	8.8	none	70.0	17.9
Alexander	T.S.	perthite	0.9	6.3	0.8	74.3	16.7
Alexander	S.F.	perthite	0.6	20.5	none	17.0	7.8
Alexander	T.S.	perthite	none	4.6	none	88.9	5.6
Alexander	S.F.	perthite	none	13.4	none	67.6	18.9
<i>N.C. Blue Ridge (Southern)</i>							
Whitehall	T.S.	pegmatite	none	20.0	0.4	71.2	8.4
Bethel	T.S.	pegmatite	none	1.6	none	76.5	21.8
Cox	S.F.	granite	22.2	32.9	4.8	1.7	39.4
<i>Georgia Piedmont</i>							
Funkhauser	S.F.	pegmatite	13.9	41.2	0.3	1.6	42.9
Funkhauser	S.F.	pegmatite	38.2	12.6	none	3.0	46.5
Funkhauser	S.F.	pegmatite	3.8	5.0	23.0	17.4	51.0

S.F.—Analysis of size fractions.

T.S.—Point-count of thin-sections.

kaolinite was 1:27 in one sample and averaged about 1:6 in those samples analyzed. Most of the feldspar alters to vermicular kaolinite through the

intermediate mica stage and the remainder alters to hydrated halloysite. The primary mica alters to vermicular kaolinite as was the case in all the deposits studied. Bulk analyses of samples from the Funkhauser Mine are listed in Table 5.

### DISCUSSION

The sequence of alteration of minerals follows that given by Goldich (1938). The plagioclase alters first, followed by potash feldspar and mica. Quartz was not altered noticeably. In thin section the feldspars are observed altered to halloysite. Remnants of the same crystal of feldspar are present in a matrix of halloysite. Remnants of feldspars, partially altered to "books" of secondary mica and kaolinite likewise were observed. The absence of fine-grained kaolinite in most of the samples was evidenced by the good agreement obtained in the same sample between the point-count method and the analysis of size fractions. In general, the "books" of mica derived from weathering of feldspar were smaller than primary mica and did not show as high a retardation. The "books" of secondary mica were not arranged parallel to each other. This resulted in a random arrangement of vermicular kaolinite aggregates as contrasted to the oriented aggregates derived from a larger "book" of primary muscovite. When the latter is kaolinized, the "books" show a parting perpendicular to the basal cleavage at 0.02 to 0.04 mm. intervals. The kaolinite was found to concentrate in this size fraction. Books of mica, which were washed thoroughly and kept in a moist condition, were found to be muscovite and kaolinite. In no such sample, even though the mica was embedded in a matrix of hydrated halloysite, was the halloysite found interleaved with the mica. The kaolinite is pseudomorphous after the mica, and the basal planes of the kaolinite orient, in general, parallel to those of the mica. Deviations occur as a result of parting and a curving of the vermicular kaolinite aggregates as the mica is altered. The interleaving of the mica and kaolinite was on a gross scale; no mixed-layer effects were observed.

Residual kaolin clays derived from feldspathic rocks in the Southern Appalachian show a general increase in the content of hydrated halloysite southward from Virginia into North Carolina where a maximum of hydrated halloysite is noted in the Spruce Pine district. Southward from this district to the southern end of the Appalachian chain, there is a general decrease in the amount of hydrated halloysite until at the southernmost deposit studied, kaolinite predominates. Although these are the general trends, locally there are exceptions, since primary mica content, topographic expression, drainage and vegetation cover are all influencing factors in addition to that of overall climate.



Hydrated halloysite, as observed, had formed by the weathering of feldspars. No transitions between hydrated halloysite and kaolinite were evident. Effective leaching from the feldspar of all of its bases probably destroys its structure and the colloidal silica and alumina are arranged into the random structure of hydrated halloysite. It is significant that hydrated halloysite, not its dehydrated product, always was present except where samples were obtained from dried exposures. This indicates that environmental conditions conducive to the formation of hydrated halloysite have not changed appreciably since Tertiary time. The stability of hydrated halloysite up to 100° C. was determined by Sand (1952). The boundary curve delineating the stable field for hydrated halloysite follows fairly closely the vapor pressure-temperature curve of water. Although hydrated halloysite does dehydrate rather easily as reported by MacEwan (1946), Brindley and Goodyear (1948) and others, it can exist to relatively high temperatures as shown by Roy and Osborn (1954). Hydrated halloysite was not observed to coexist at equilibrium in various proportions with halloysite at various humidities as has been reported. Theoretically, only on the univariant boundary curve can they coexist as stable phases, presuming a starting material of pure hydrated halloysite. If halloysite is present in a sample of hydrated halloysite due to partial dehydration, then halloysite will coexist with the hydrated form since the reaction is irreversible. Brindley also proposes the phenomenon of entrapped pockets of hydrated halloysite present in halloysite.

No matter what the intensity of leaching, even where the feldspars alter completely to hydrated halloysite, the primary muscovite mica always alters to kaolinite. Thus, in a completely weathered perthite crystal, patches of vermicular kaolinite derived from the disseminated mica "books" occur in a matrix of hydrated halloysite. This is an apparent anomaly which can be explained only on the basis of structural control. Once the feldspar alters to secondary mica, the compositional and structural control, evidently imposed by the mica, causes vermicular kaolinite to be the next weathering product. A completely leached and hydrated muscovite has the same ratio of alumina, silica and water as kaolinite, but the mechanism of transfer of silicon and aluminum from a 2:1 layer structure to a 1:1 type is unknown. The vermicular kaolinite in these deposits usually is not present in size fractions below two microns; a relatively pure hydrated halloysite can be obtained by fractionation.

The nature of the clay end product resulting from the weathering of feldspathic rocks in this region is believed to be a function of mineral composition, rock texture, degree of fracturing, topographic expression,

vegetation cover and climate. Where conditions favor the formation of hydrated halloysite, a feldspathic rock high in mica content yields a kaolin clay correspondingly high in kaolinite. Conversely, a rock low in mica yields a clay high in content of hydrated halloysite. For this reason, some samples are lower in hydrated halloysite content in the Spruce Pine district as compared to some pegmatitic samples from the Piedmont. Rock texture and degree of fracturing determine the drainage pattern. Where vegetation cover was sparse a tendency toward formation of secondary mica was noted. River terraces apparently are favorable locations for the formation of extensive deposits of hydrated halloysite. Good drainage effects a thorough leaching of potash and inhibits the formation of secondary mica.

This work concurs with the early views of Selle and others that secondary mica is an essential intermediate product in the formation of residual kaolinite from feldspar.

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# AMBLYGONITE, CASSITERITE, AND ASSOCIATED MINERALS FROM CÁCERES, WESTERN SPAIN

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## ABSTRACT

A detailed description of the physical and chemical properties of amblygonite ( $\text{montebrasite}$ ,  $\text{LiAl}(\text{OH}, \text{F})\text{PO}_4$ ) from Cáceres, Western Spain, is given. The amblygonite occurs in pneumatolytic tin veins. Associated minerals include quartz, cassiterite, muscovite, apatite, and the sulfides stannite, chalcopyrite, sphalerite, and arsenopyrite. Feldspar is absent.

A new occurrence of the rare phosphate minerals augelite ( $\text{Al}_2\text{PO}_4(\text{OH})_3$ ) and childrenite ( $(\text{Fe}, \text{Mn})\text{AlPO}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$ ) has been found.

Cassiterite from two localities of Cáceres province has been analyzed by chemical and quantitative spectrochemical methods. Special attention has been paid to the presence of titanium, columbium, and tantalum.

## INTRODUCTION

Amblygonite has been found at several localities in Western Spain, associated with tin deposits. In the following, the amblygonite of the two occurrences near Cáceres ( $39^\circ 28' \text{N}$ ,  $6^\circ 22' \text{W}$ ) will be described. One of the deposits is situated 6 miles S. of Cáceres at the locality called Tráquilón. The lithium mineral occurs in veins which invade a body of altered muscovite-rich granite, a mile in diameter. The granite bears tourmaline and sporadically torbernite. The veins are no more than one to three feet thick and composed chiefly of quartz and amblygonite with subordinate cassiterite and minor apatite, whereas feldspar is absent. In some of the veins extremely fine grained muscovite resembling wax replaces all the other minerals. It is of later origin. Roberts (1948) reported a similar occurrence from Uganda.

The rare phosphates augelite, childrenite, and pseudomalachite ( $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ ) have been found for the first time at Tráquilón. Several sulfides are imbedded in the quartz and amblygonite. They include stannite (common variety, an isotropic and a pink variety. An account of the different varieties of stannite is given by Ramdohr (1944)), chalcopyrite, sphalerite, arsenopyrite, pyrite, covellite, pyrrhotite, and bismuth.

Amblygonite and cassiterite have been mined, the latter mainly from placers.

The second occurrence of amblygonite lies 3 miles SE of Cáceres and is called Valdeflores. It is very similar to the first one, but the veins are intrusive into tourmalinized schists of Silurian Age. The tourmalinization is prior to the formation of the deposit. Muscovite, often referred to as pyrophyllite, is abundant in all the veins. Under the microscope flaky

masses of this mineral are seen to replace quartz, amblygonite, apatite, and cassiterite. At present only the latter is being mined.

An unusual occurrence of a white clay mineral has been found in one of the veins of Valdeflores. It consists of about 60% "fireclay," decomposed feldspar, and montmorillonite. The apatite contains up to 0.3% manganese, is bluish, and sometimes globular with a radiating subfibrous structure (see Fig. 1). No rare phosphates have been found here.

Cassiterite as well as wolframite are widespread in Western Spain, but they are not associated with each other in the deposits described here. The cassiterite from the amblygonite deposit of Trasquilón and the

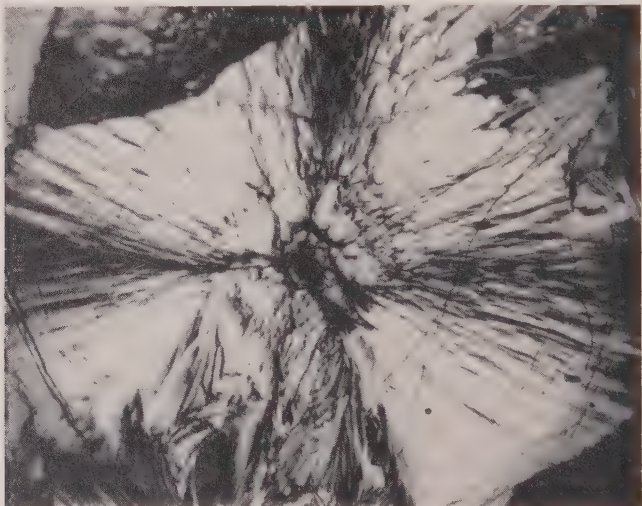


FIG. 1. Globular apatite showing radiating structure, with some muscovite. Crossed nic.,  $\times 24$ . Valdeflores.

cassiterite from Logrosán, 50 miles ESE of Cáceres, still in Cáceres province, will be studied. At Logrosán a body of granitic rock outcrops, 1 mile in diameter, forming a steep hill. It is invaded by many tin-bearing quartz veins, the richest being only a few inches thick. Generally the cassiterite is massive, but sporadically well-developed crystals are imbedded in the clay of the veins. Amblygonite, apatite, and autunite have been found. The sulfides found at Trasquilón could be detected here as well. Muscovite is frequent in the contact with the wall-rock. The tin is being mined.

#### AMBLYGONITE

The amblygonite or more exactly, montebrasite, from both Trasquilón and Valdeflores is massive. No crystals have been found. It is white with

patches of greenish-blue due to a copper content of about 0.001–0.01%. Polysynthetic twinning on  $(\bar{1}\bar{1}1)^*$  is developed in all the thin sections examined. A rectangular structure due to two sets of microscopic lamellar twinning is frequent (see Fig 2). On the universal stage it could be shown that the two sets of lamellae are twinned on the same law  $(\bar{1}\bar{1}1)$ , but with different composition planes, namely  $(\bar{1}\bar{1}1)$  and an irregular plane.

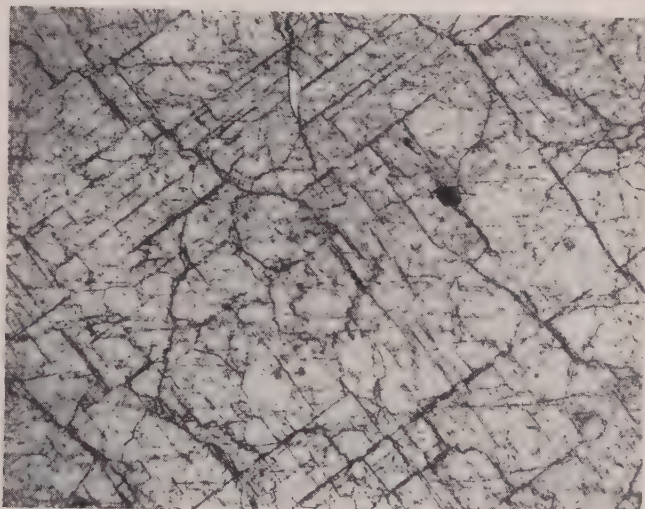


FIG. 2. Amblygonite showing rectangular structure due to twinning on  $(\bar{1}\bar{1}1)$ . Crossed nic.,  $\times 24$ . Trasquilón.

TABLE 1. THE OPTICAL PROPERTIES OF THE MONTEBRASITE FROM TRASQUILÓN (6 Miles S. of Cáceres, W. Spain)

$\alpha$ (Na)	1.612		$\phi$	$\rho$
$\beta$	1.620 (calculated 1.621)	X	$23^\circ$	$62^\circ$
$\gamma$	1.635	Y	$-80^\circ$	$68^\circ$
(correct to 0.001)		Z	$158^\circ$	$38^\circ$
$2V_\gamma$	$78^\circ$ (correct to $2^\circ$ )			(correct to $2^\circ$ )

### Optical Properties

The refractive indices were determined by means of suitable immersion liquids on the universal stage.

In thin section two cleavage directions are represented which are  $(100)$  and  $(0\bar{1}1)$ , with  $(100)$  being perfect. By means of these cleavages the

\* Crystallographic orientation proposed by Richmond and Wolfe (1943).



TABLE 2. NEW DETERMINATIONS OF THE OPTICAL ORIENTATION OF AMBLYGONITE

	$\phi$			$\rho$		
	I	II	III	I	II	III
X	19°	19°	23°	83°	69°	62°
Y	-72°	-78°	-80°	69°	72°	68°
Z	130°	156°	158°	21°	28°	38°

I. Hebron, Maine, USA.

Fluorine content 5.45% (Palache 1943).

II. Karibib, SW. Africa.

Fluorine content 5.40% (Nel 1946).

III. Trasquilón, Cáceres, W. Spain

Fluorine content 1.13%

optical orientation of the amblygonite from Trasquilón was established on the universal stage. So far the optical orientation of fluorine-poor amblygonite has never been exactly determined. The data given by Pehrman (1945) for montebrasite from Kimito (Finland) with 0.57% fluorine are erroneous, because he used erroneous cleavages based on the old data of Dana. Transforming Pehrman's values, the writer obtained

TABLE 3. CHEMICAL AND SPECTROCHEMICAL ANALYSIS (BY THE AUTHOR) OF THE MONTEBRASITE FROM CÁCERES (W. SPAIN)

Montebrasite from Trasquilón (6 miles S. of Cáceres)				Montebrasite from Valdeflores (3 miles SE. of Cáceres)			
Li <sub>2</sub> O	9.57	<i>Formula</i>		Li <sub>2</sub> O	9.22	<i>Formula</i>	
Na <sub>2</sub> O	0.11	Li, Na	1.91	Na <sub>2</sub> O	0.59	Li, Na	1.91
Al <sub>2</sub> O <sub>3</sub>	34.7	Al	2.02	Al <sub>2</sub> O <sub>3</sub>	34.4	Al	2.03
P <sub>2</sub> O <sub>5</sub>	48.0	P	2.01	P <sub>2</sub> O <sub>5</sub>	47.3	P	2.00
H <sub>2</sub> O	6.4	OH, F	2.00	H <sub>2</sub> O	5.2	OH, F	2.00
F	1.13	O	8.00	F	4.40	O	8.00
Rem.	0.26	H <sub>2</sub> O	0.14	Rem.	0.45	H <sub>2</sub> O	0.21
	100.17				101.56		
F=O	0.48	OH:F=10:1		F=O	1.85	OH:F=2:1	
Total	99.69			Total	99.71		
Rem: MgO	0.1			Rem: MgO	0.2		
SiO <sub>2</sub>	0.05			SiO <sub>2</sub>	0.1		
SnO <sub>2</sub>	0.06			SnO <sub>2</sub>	0.02		
TiO <sub>2</sub>	0.05			TiO <sub>2</sub>	0.13		
In terms of the end members:				In terms of the end members:			
Montebrasite		91%		Montebrasite		65%	
Amblygonite		9%		Amblygonite		35%	

nearly the same orientation as that given below for the amblygonite from Trasquilón.

### *Chemical Properties*

The amblygonite is not quite free from impurities. Under the microscope very small inclusions are seen which are probably muscovite.

The fluorine was determined by the distillation method. A spectrogram revealed the presence of noteworthy amounts of magnesium, silicon, tin, and titanium. With the exception of titanium they were determined spectrochemically. Cathode layer excitation was used with iron as an internal standard. The values are correct to about 30%. The silicon content is obviously due to the inclusions. The determination of titanium was made by the colorimetric method after separation of the fluorine.

### AUGELITE AND CHILDRENITE

A new occurrence of augelite and childrenite has been found in the amblygonite veins at Trasquilón. Augelite occurs in tabular crystals



FIG. 3. Augelite laths imbedded in impure amblygonite. Crossed nic.,  
×24. Trasquilón.

intergrown with amblygonite (see Fig. 3). Well-developed but superficially greenish (due to copper) and dull crystals were discovered in a geode (see Fig. 4). On the universal stage the same optical properties were found as reported by Peacock and Moddle (1941).

Childrenite has been found only in some druses as small, brittle, long



FIG. 4. Tabular crystals of augelite on quartz, with some acicular apatite.  $\times 2$ . Trasquilón.

prismatic crystals, color brownish. The childrenite could be verified by an  $x$ -ray powder pattern. On the universal stage the following optical data (Table 4) were determined. Material is too scarce for chemical analysis.

TABLE 4. OPTICAL DATA OF THE CHILDRENITE FROM TRASQUILÓN  
(6 Miles S. of Cáceres, W. Spain)

$\alpha$ (Na)	1.647	$2V_{\alpha}$ $33^{\circ}$ (correct to $2^{\circ}$ )
$\beta$ calculated	1.669	
$\gamma$	1.671	Dispersion $r > v$ , strong
(correct to 0.001)		

#### CASSITERITE

At Trasquilón the cassiterite is imbedded in quartz and amblygonite along the contacts of the veins. In the hand specimen it is nearly black and in thin section highly pleochroic with  $\omega$  green and  $\epsilon$  red. All the crystals are twinned and show marked zonal banding (see Fig. 5).

At Logrosán excellent crystals of cassiterite are found in veins where the quartz is replaced by clay. They are brown and less pleochroic with complex twinning and zonal structure.

The chemical properties of the cassiterite have been studied in detail by spectrochemical methods. For the determination of iron, columbium, and tantalum cathode layer excitation was employed. Tin served as an



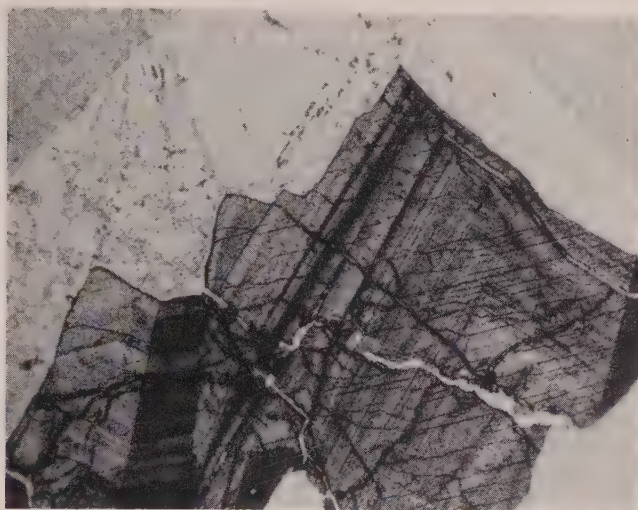


FIG. 5. Zonal cassiterite showing twinning and pleochroism, with muscovite penetration. One nic.,  $\times 24$ . Trasquilón.

internal standard for iron, and iron as an internal standard for columbium and tantalum. The lines used for columbium and tantalum were Cb I 2657.616, Ta I 2653.274, and Fe I 2651.706 (internal standard line). The accuracy obtained is not too high, perhaps between 20 and 30%. The presence of scandium, molybdenum, and tungsten could not be established in the spectrograms. The determination of titanium was made by the colorimetric method.

TABLE 5. CHEMICAL AND SPECTROCHEMICAL ANALYSIS (BY THE AUTHOR) OF CASSITERITE FROM CÁCERES PROVINCE (W. SPAIN)

Cassiterite from Trasquilón (6 miles S. of Cáceres)				Cassiterite from Logrosán (50 miles ESE. of Cáceres)			
		<i>Formula</i>				<i>Formula</i>	
SnO <sub>2</sub>	97.5	Sn	0.966	SnO <sub>2</sub>	97.5	Sn	0.960
Fe <sub>2</sub> O <sub>3</sub>	1.0	Fe	0.019	Fe <sub>2</sub> O <sub>3</sub>	0.3	Fe	0.006
TiO <sub>2</sub>	0.2	Ti	0.004	TiO <sub>2</sub>	1.5	Ti	0.028
Cb <sub>2</sub> O <sub>5</sub>	0.7	Cb	0.008	Cb <sub>2</sub> O <sub>5</sub>	0.5	Cb	0.006
Ta <sub>2</sub> O <sub>5</sub>	0.7	Ta	0.005	Ta <sub>2</sub> O <sub>5</sub>	0.02	O	2.000
Total	100.1	O	2.000	Total	99.8		

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# SOLVENTS AND SOLUTES FOR THE PREPARATION OF IMMERSION LIQUIDS OF HIGH INDEX OF REFRACTION\*

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## ABSTRACT

The types of compounds that should be suitable as solvents and solutes for the preparation of immersion liquids of high index of refraction are covalent inorganic, organic, and metal-organic compounds containing the nonmetallic elements of the carbon, nitrogen, oxygen, and fluorine groups of the periodic table, and mercury and thallium. Many of these compounds have already been used to make immersion liquids of high index of refraction. Other compounds of these types that might be suitable are suggested.

Most of the developmental work on immersion liquids of high index of refraction has generally been either one of trial and error or an extension of an earlier experimenter's work. The purpose of this paper is to define the types of inorganic and organic compounds that are most likely to be suitable as solvents and solutes in the preparation of liquids of high index of refraction. Practical considerations such as solubility, stability, and toxicity will limit the use of individual compounds and small groups of compounds although their indices of refraction may be high. Déverin (1934) has listed 12 extensive groups of organic compounds which he considered fertile fields for investigation because these groups of compounds would tend to have relatively high indices of refraction.

Liquids of high index of refraction will generally be composed of substances that have high indices of refraction. In the preparation of these liquids the solvent should be a liquid of relatively high index of refraction, or a solid of high index of refraction whose melting point is very close to room temperature, so that if one dissolves some solute in it, the freezing point will be depressed below room temperature and a liquid will result. Of all the elements, white phosphorus (melting point, 44° C.) is the only one that can and has been used as a solvent to prepare a liquid of high index of refraction. (For references, see Meyrowitz, 1955.)

The low-melting inorganic compounds will generally be covalent or nonpolar. Covalent compounds are those in which the bonds holding the atoms together are formed by the sharing of electrons. Covalent compounds are not electrical conductors in the liquid state, either when pure or dissolved in a suitable solvent (Glasstone, 1946, p. 66), and they have low melting and boiling points because the external fields of force which

\* Publication authorized by the Director, U. S. Geological Survey.

exist between the molecules in the solid state are small (Glasstone, 1946, p. 67). They are also generally soluble in organic compounds.

Covalent inorganic compounds are usually composed of elements whose electronegativities are of the same magnitude. Electronegativity is defined as the power of an atom in a molecule to attract electrons to itself (Pauling, 1940, p. 58). As the difference in electronegativity of the atoms in a molecule decreases, the molecule becomes more covalent. Stable compounds composed of atoms having electronegativity values of the same magnitude are found primarily among the nonmetallic group of atoms (the carbon, nitrogen, oxygen, and fluorine groups of the periodic table).

Compounds that have both low melting points (close to room temperature) and high indices of refraction are generally composed of these elements. Examples are (1) arsenic tribromide,  $\text{AsBr}_3$ , melting point  $33^\circ \text{C.}$ , (2) selenium monobromide,  $\text{Se}_2\text{Br}_2$ , liquid at room temperature, and (3) stannic bromide,  $\text{SnBr}_4$ , melting point  $31^\circ \text{C.}$  Two of these compounds, namely arsenic tribromide and selenium monobromide, have been used as solvents to prepare immersion liquids of high index of refraction. (For references, see Meyrowitz, 1955.)

Organic compounds are generally covalent, and very many organic liquids are good solvents for covalent solids. The range of the indices of refraction of organic liquids, however, is 1.30 to 1.80 and of organic solids 1.3 to 2.5 (Weissberger, 1949, p. 1143). Relatively few of the thousands of organic liquids have indices of refraction higher than 1.74. Similarly most of the organic solids have relatively low indices of refraction. From the following empirical relations, one can define the type of organic compound that would have a high index of refraction and probably be suitable as a solvent.

The index of refraction of a compound depends upon (*a*) the elements present, (*b*) their number, and (*c*) the manner in which they are combined. The homologous series of compounds in Table 1 shows that as one element in the compound is replaced by another the index of refraction changes. The homologous series of compounds in Table 2 shows that as the number of atoms of any one element present changes, the index of refraction changes. If the replacement in a compound of one element by another results in an increase in the index of refraction, generally the addition of more atoms of the element (where possible) will increase the index of refraction. The series of compounds in Table 3, each series having the same chemical composition, show that the index of refraction also depends on the manner in which the elements are combined.



TABLE 1. SERIES OF COMPOUNDS SHOWING THE CHANGE IN INDEX OF REFRACTION AS ONE ELEMENT IN A COMPOUND IS REPLACED BY ANOTHER

Compound	Formula	$n_D$	Reference
Arsenic trihydride	AsH <sub>3</sub>	gas	Lange, 1949, p. 186
Arsenic trichloride	AsCl <sub>3</sub>	1.62	Hodgman, 1950, p. 456
Arsenic tribromide	AsBr <sub>3</sub>	1.78 (24° C.)	Borgström, 1929, p. 59
Arsenic triiodide	AsI <sub>3</sub>	solid	Lange, 1949, p. 186
Phosphorus trihydride	PH <sub>3</sub>	gas	Lange, 1949, p. 248.
Phosphorus trichloride	PCl <sub>3</sub>	1.52	Lange, 1949, p. 1012
Phosphorus tribromide	PBr <sub>3</sub>	1.70	Lange, 1949, p. 1012
Phosphorus triiodide	PI <sub>3</sub>	solid	Lange, 1949, p. 250
Phosphorus trichloride	PCl <sub>3</sub>	1.52	Lange, 1949, p. 1012
Arsenic trichloride	AsCl <sub>3</sub>	1.62	Hodgman, 1950, p. 456
Antimony trichloride	SbCl <sub>3</sub>	solid	Lange, 1949, p. 184
Methane	CH <sub>4</sub>	gas	Lange, 1949, p. 561
Methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	1.42	Lange, 1949, p. 1007
Methylene bromide	CH <sub>2</sub> Br <sub>2</sub>	1.55	Timmermans, 1950, p. 216
Methylene iodide	CH <sub>2</sub> I <sub>2</sub>	1.74	Lange, 1949, p. 1007
Benzene	C <sub>6</sub> H <sub>6</sub>	1.50	Lange, 1949, p. 943
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	1.53	Lange, 1949, p. 949
Bromobenzene	C <sub>6</sub> H <sub>5</sub> Br	1.56	Lange, 1949, p. 945
Iodobenzene	C <sub>6</sub> H <sub>5</sub> I	1.62	Lange, 1949, p. 989
Naphthalene	C <sub>10</sub> H <sub>8</sub>	1.58 (98° C.)	Lange, 1949, p. 1007
$\alpha$ -Chloronaphthalene	C <sub>10</sub> H <sub>7</sub> Cl	1.63	Lange, 1949, p. 950
$\alpha$ -Bromonaphthalene	C <sub>10</sub> H <sub>7</sub> Br	1.66	Lange, 1949, p. 945
$\alpha$ -Iodonaphthalene	C <sub>10</sub> H <sub>7</sub> I	1.71	Lange, 1949, p. 989
Tetramethyl silicon	(CH <sub>3</sub> ) <sub>4</sub> Si	1.359	Beilstein, 1929, p. 579
Tetramethyl germanium	(CH <sub>3</sub> ) <sub>4</sub> Ge	1.387	Beilstein, 1942, p. 1008
Tetramethyl tin	(CH <sub>3</sub> ) <sub>4</sub> Sn	1.520	Beilstein, 1922, p. 632
Tetramethyl lead	(CH <sub>3</sub> ) <sub>4</sub> Pb	1.512	Heilbron and Bunbury, 1943, p. 502
Tetraethyl silicon	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Si	1.425	Beilstein, 1929, p. 580
Tetraethyl germanium	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Ge	1.44	Beilstein, 1942, p. 1008
Tetraethyl tin	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Sn	1.514	Beilstein, 1922, p. 632
Tetraethyl lead	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Pb	1.514	Beilstein, 1922, p. 638

TABLE 2. SERIES OF COMPOUNDS SHOWING CHANGE IN INDEX OF REFRACTION AS ELEMENT NUMBER CHANGES

Compound	Formula	$n_D$	Reference
Benzene	$C_6H_6$	1.50	Lange, 1949, p. 943
Chlorobenzene	$C_6H_5Cl$	1.53	Lange, 1949, p. 949
<i>o</i> -Dichlorobenzene	$C_6H_4Cl_2$	1.55	Lange, 1949, p. 954
Trichlorobenzene	$C_6H_3Cl_3$	1.57	Lange, 1949, p. 1020
Diethyl sulfide	$(C_2H_5)_2S$	1.44	Mumford and Phillips, 1950, p. 80
2:2 Dichlorodiethyl sulfide	$(C_2H_4Cl)_2S$	1.53	Mumford and Phillips, 1950, p. 80
1:1:2:2:2 Hexachlorodiethyl sulfide	$(C_2H_2Cl)_2S$	1.57	Mumford and Phillips, 1950, p. 80

The particular elements present in a compound have a much greater effect on the index of refraction of the compound than the manner in which these elements are combined. The increase in index of refraction

TABLE 3. INDICES OF REFRACTION OF SEVERAL SERIES OF COMPOUNDS, THE COMPOUNDS IN EACH SERIES HAVING THE SAME CHEMICAL COMPOSITION

Compound	Formula	$n_D$	Reference
Dipropargyl	$C_6H_6$	1.44	Lange, 1949, p. 969
Benzene	$C_6H_6$	1.50	Lange, 1949, p. 943
tert-Butyl chloride	$C_4H_9Cl$	1.387	Lange, 1949, p. 946
sec-Butyl chloride	$C_4H_9Cl$	1.395	Lange, 1949, p. 946
iso-Butyl chloride	$C_4H_9Cl$	1.397	Lange, 1949, p. 946
<i>n</i> -Butyl chloride	$C_4H_9Cl$	1.402	Lange, 1949, p. 946
<i>p</i> -Dibromobenzene	$C_6H_4Br_2$	1.574	Lange, 1949, p. 953
<i>m</i> -Dibromobenzene	$C_6H_4Br_2$	1.608	Lange, 1949, p. 953
<i>o</i> -Dibromobenzene	$C_6H_4Br_2$	1.612	Lange, 1949, p. 953
Bromopropylene (2)	$C_3H_5Br$	1.447	Lange, 1949, p. 945
Bromopropylene ( $\alpha$ )	$C_3H_5Br$	1.455	Lange, 1949, p. 945
Allyl bromide	$C_3H_5Br$	1.514	Lange, 1949, p. 940
Propionic acid	$C_3H_6O_2$	1.387	Lange, 1949, p. 1013
Methyl acetate	$C_3H_6O_2$	1.359	Lange, 1949, p. 992
Ethyl formate	$C_3H_6O_2$	1.360	Lange, 1949, p. 977
Acetol	$C_3H_6O_2$	1.430	Lange, 1949, p. 938

that is obtained by replacing one element of a compound by another suitable one is usually relatively large (a few units in the first decimal place, Table 1) as compared to the increase obtained by changing the manner in which the elements of a compound are combined (a few units in the second decimal place, Table 3). Inasmuch as it is desirable to use compounds having the highest practical indices of refraction in the preparation of immersion liquids of high index of refraction and inasmuch as changes in molecular structure affect the index of refraction to a relatively small extent, the discussion of changes in molecular structure as they affect the index of refraction will be omitted.

A metal-organic compound will generally have a much higher index of refraction than the organic compound from which it is derived. (See Table 1.)

If an element in any given compound is replaced by a denser element that belongs to the same group in the periodic table, there will usually be an increase in the index of refraction of the new compound as compared to the previous one. Increases in density, melting point, and boiling point generally accompany the increase in index of refraction. However, the advantage of an increase in index of refraction which results from the replacement of one element by another may be of no value in the search for a suitable solvent, because the melting point of the new compound may be considerably higher than room temperature. This is illustrated in inorganic compounds by the following series of compounds:

Compound	Formula	$n_D$	Reference	Melting point, ° C.	Reference
Arsenic trichloride	AsCl <sub>3</sub>	1.62	Hodgman, 1950, p. 456	-18	Lange, 1949, p. 187
Arsenic tribromide	AsBr <sub>3</sub>	1.78	Borgström, 1929, p. 59	31	Lange, 1949, p. 187
Arsenic triiodide	AsI <sub>3</sub>	$\omega = 2.59$ $\epsilon = 2.23$	Lange, 1949, p. 899	146	Lange, 1949, p. 187
Phosphorus tribromide	PBr <sub>3</sub>	1.70	Lange, 1949, p. 1012	-40	Lange, 1949, p. 249
Arsenic tribromide	AsBr <sub>3</sub>	1.78	Borgström, 1929, p. 59	31	Lange, 1949, p. 187
Antimony tribromide	SbBr <sub>3</sub>	— <sup>1</sup>	Slawson, 1922, p. 175	96.6	Lange, 1949, p. 185

<sup>1</sup> " . . . the indices of refraction were considerably higher than that of the liquid (1.74)."

and in organic compounds by these series of compounds:

Compound	Formula	$n_D$	Reference	Melting point, ° C.	Reference	Boiling point, ° C.	Reference
Chloroform	$\text{CHCl}_3$	1.46	Lange, 1949, p. 950	-63.5	Lange, 1949, p. 427		
Bromoform	$\text{CHBr}_3$	1.60	Lange, 1949, p. 945	8-9	Lange, 1949, p. 405		
Iodoform	$\text{CHI}_3$	$\omega = 2.11$ $\epsilon = 1.77$	West, 1937, p. 463-464	119	Lange, 1949, p. 553		
Dichloromethylarsine	$\text{CH}_2\text{AsCl}_2$	1.57	Beilstein, 1942, p. 979	— <sup>1</sup>	Beilstein, 1942, p. 979	133 (760 mm.)	Beilstein, 1942, p. 979
Dichloromethylstibine	$\text{CH}_2\text{SbCl}_2$	— <sup>1</sup>		— <sup>2</sup>	Friend, 1936, p. 184	115-120 (60 mm.)	Friend, 1936, p. 184
Dichloromethylbismuthine	$\text{CH}_2\text{BiCl}_2$	— <sup>1</sup>		242	Friend, 1936, p. 269-270		

<sup>1</sup> Not available.

<sup>2</sup> Does not solidify at approximately 0° C.

Although arsenic triiodide, antimony tribromide, iodoform, and dichloromethylbismuthine have or should have high indices of refraction, they could not be used as solvents because their melting points are much higher than room temperature. With these counterbalancing factors of increase in index of refraction and increase in melting point in mind, one can say that the types of organic compounds that would be suitable as solvents for the preparation of immersion liquids of high index of refraction would be organic or metal-organic compounds containing arsenic in preference to bismuth, sulfur in preference to tellurium, and bromine in preference to iodine. These preferences would tend to insure a low-melting compound. The organic part of the compound should be as small as possible so that the highest possible index of refraction be obtained.

Organic and metal-organic compounds that have been used as solvents (for reference, see Meyrowitz, 1955) are:

1.  $\alpha$ -Bromonaphthalene,  $\text{C}_{10}\text{H}_7\text{Br}$
2. Cacodyl selenide,  $[(\text{CH}_3)_2\text{As}]_2\text{Se}$
3. Carbon disulfide,  $\text{CS}_2$
4. Diethylselenium,  $(\text{C}_2\text{H}_5)_2\text{Se}$
5. Dimethylmercury,  $(\text{CH}_3)_2\text{Hg}$
6.  $\alpha$ -Iodonaphthalene,  $\text{C}_{10}\text{H}_7\text{I}$
7. Methylene iodide,  $\text{CH}_2\text{I}_2$
8. Phenyl-di-iodoarsine,  $\text{C}_6\text{H}_5\text{AsI}_2$



It has been shown that the compounds, both inorganic and organic, that would be suitable for use as solvents would tend to be essentially covalent. Nonpolar or covalent solvents generally dissolve only nonpolar or covalent solutes. Solid compounds (as distinguished from low-melting solids) that are essentially covalent, that is, compounds containing weakly polar parts, would tend to be soluble in covalent inorganic, organic, and metal-organic compounds.

Some free elements are soluble in covalent solvents. They are found among the nonmetallic elements. The elements that have already been used as solutes (for references, see Meyrowitz, 1955) are:

1. Arsenic
2. Iodine
3. Phosphorus
4. Selenium
5. Sulfur

Although tellurium tends to be metallic, it might be possible to find a solvent containing one or more substances in which appreciable amounts of the brown amorphous form of tellurium would be soluble.

The covalent inorganic compounds will usually be composed of the nonmetallic elements (the carbon, nitrogen, oxygen, and fluorine groups of the periodic table). Mercury and thallium should be included among these elements because they can form covalent compounds (Partington, 1950, p. 770, 805).

The inorganic compounds that have already been used as solutes (for references, see Meyrowitz, 1955) are:

1. Antimony tribromide,  $\text{SbBr}_3$
2. Antimony triiodide,  $\text{SbI}_3$
3. Antimony trisulfide,  $\text{Sb}_2\text{S}_3$
4. Arsenic disulfide,  $\text{As}_2\text{S}_2$
5. Arsenic triiodide,  $\text{AsI}_3$
6. Arsenic trisulfide,  $\text{As}_2\text{S}_3$
7. Mercuric iodide,  $\text{HgI}_2$
8. Mercuric sulfide,  $\text{HgS}$
9. Stannic iodide,  $\text{SnI}_4$

The types of organic compounds that would be suitable as solutes will be similar to those that would be suitable as solvents except that the inorganic and halogen portion of the compounds would be increased as much as possible and the organic portion of the molecule kept as small as possible. The limiting factor in the consideration of the compounds suitable for use as solvents is the melting point. Any change in the composition of a compound made in order to increase its index of refraction is to no advantage if the melting point of the new compound is much

above room temperature. The limiting factor for the solutes (inorganic as well as organic) is its solubility in the solvent.

As the melting points increase in a homologous series of compounds in which an element is replaced by another in the same group of the periodic table, there will generally be a decrease in the covalent properties of the compounds. This will usually result in a decrease in the solubility of the compounds in covalent solvents. The advantage of an increase in index of refraction will be of no practical value, if by replacing one element of a compound by another, we decrease the covalent character of the compound and so decrease to a large extent the solubility of the compound.

Organic compounds that have been used as solutes are:

1. Iodoform,  $\text{CHI}_3$ .
2. Tetraiodoethylene,  $\text{C}_2\text{I}_4$  (for references, see Meyrowitz, 1955). It will be noticed that the halogen fraction of the total mass of each of these two compounds is relatively large compared to the organic fraction.

The use of these types of covalent compounds which should be suitable as solvents and solutes for the preparation of immersion liquids of high index of refraction will be circumscribed by their instability, toxicity, and reactivity to the immersed phase.

It would be useful in the consideration of compounds for possible use as solvents and solutes for the preparation of immersion liquids of high index of refraction to have available their indices of refraction. Much of these data is not readily available, for a search of the chemical literature (especially that previous to the last 20 to 30 years) will reveal that the indices of refraction of relatively few organic and metal-organic solid compounds are recorded. The indices of refraction of many more liquid compounds than of solid compounds are given in the literature.

The index of refraction of a compound can be calculated by means of the Lorentz-Lorenz equation

$$R_D = \frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M}{d}$$

where ( $R_D$ ) is the molar refraction for the  $D$  line of sodium,  $n_D$  is the index of refraction for the  $D$  line of sodium, ( $M$ ) is the molecular weight, and ( $d$ ) is the density; ( $n_D$ ) and ( $d$ ) are measured at the same temperature.

The molar refraction of compounds is usually not available, whereas the density is frequently available. However, the molar refraction of a compound can be calculated using the values for bond refractions, and in turn the index of refraction can be calculated with a reasonable degree of accuracy from the molecular refraction and density data.

The molar refraction is a physical property which is additive as well as constitutive, that is to say, the molar refraction of a molecule depends

not only upon the number and kind of atoms present, but also upon the particular arrangement of the atoms within the molecule. The molar refraction of a compound can be considered as the sum of the refractions of the atoms in the molecule. To each of the component atoms is assigned a definite part of this total refraction, and this part is referred to as the atomic refraction. However, inasmuch as the atomic refraction depends on the manner in which the atom is held in the molecule, it is more accurate to divide the molar refraction into bond refractions or electron groups refractions.

Although there is often no exact additivity of the bond refractions,

TABLE 4. EMPIRICAL AND CALCULATED INDICES OF REFRACTION OF SOME CHEMICAL COMPOUNDS

Compound	Formula	$M$	$R_D$	$d$	° C.	Empirical $n_D$	° C.	Calculated $n_D$	Melting point ° C.
1-Chloro-5-iodopentane	$C_5H_{10}ClI$	232.50	43.06	1.6789 <sup>1</sup>	25	1.5297 <sup>1</sup>	25	1.5252	
Dimethyl tin diiodide	$Sn(CH_3)_2I_2$	402.59	54.22	2.8582 <sup>2</sup>	39.3	1.6906 <sup>2</sup>	39.3	1.7137	
Germane, tetramethylsulfide	$Ge(SCH_3)_4$	261.00	66.63	1.4364 <sup>3</sup>	25	1.6379 <sup>3</sup>	25	1.6544	
Iodoform	$CHI_3$	393.78	45.51	4.008 <sup>4</sup>	20	2.00*		1.89	119 <sup>4</sup>
Pentabromoethane	$C_2HBr_5$	424.61	49.92	3.312 <sup>5</sup>		—		1.71	56–57 <sup>5</sup>
1-Chloro-1,1,2,2-tetrabromoethane	$C_2HBr_4Cl$	380.15	47.04	3.366 <sup>5</sup>	16	—		1.77	32–33 <sup>5</sup>

$$* \bar{n} \text{ (mean) calculated using } \bar{n} = \frac{2\omega + \epsilon}{2} = 2.00 \quad \left\{ \begin{array}{l} n_\omega = 2.11 \\ n_\epsilon = 1.77 \end{array} \right\}^6$$

$$\bar{n} = \sqrt[3]{\omega^2 \epsilon} = 1.99$$

<sup>1</sup> Huber, 1951, p. 2731.

<sup>2</sup> Friend, 1928, p. 371.

<sup>3</sup> Johnson, 1951, p. 292–293.

<sup>4</sup> Hodgman, 1950, p. 949.

<sup>5</sup> Beilstein, 1918, p. 95.

<sup>6</sup> West, 1937, p. 463–464.

the deviations are so small as to be negligible in the application of these principles to the estimation of the order of magnitude of the index of refraction of a compound. A more detailed discussion of the Lorentz-Lorenz molar refraction, its additivity, and its limitations is given in Weissberger (1949, p. 1157–1177).

The molar refraction ( $R_D$ ), density ( $d$ ), index of refraction (empirical), and index of refraction (calculated using the Lorentz-Lorenz formula) of six compounds are listed in Table 4. The molar refraction was calculated using values for the bond refractions as given by Vogel et al. (1950) and Cresswell et al. (1953).

The agreement between the empirical and calculated indices of refraction of the first four compounds is relatively good. The last two com-

pounds, if stable, should be good solvents for they resemble bromoform and acetylene tetrabromide. Their indices of refraction as calculated by the Lorentz-Lorenz formula are relatively high, and their melting points are not very much above room temperature.

Other compounds that might be suitable as solvents and solutes are listed below.

Compound	Formula	Melting point ° C.	Reference
Phosphorus sesquisulfide	$P_4S_3$	172	Hodgman, 1950, p. 539
Phosphorus pentasulfide	$P_2S_5(P_4S_{10})$	276	Hodgman, 1950, p. 539
Stannic bromide	$SnBr_4$	31	Hodgman, 1950, p. 587
Methyltintribromide	$Sn(CH_3)Br_3$	50-55	Friend, 1928, p. 312
Methyltintriiodide	$Sn(CH_3)I_3$	82-85	Friend, 1928, p. 312
Diphenyltin dibromide	$Sn(C_6H_5)_2Br_2$	38	Friend, 1928, p. 324
Diiodo-p-iodophenylarsine	$(IC_6H_4)AsI_2$	80	Friend, 1930, p. 120
Bisdimethylstibine trisulfide	$[(CH_3)_2SbS]_2S$	76-78	Friend, 1936, p. 187
Diiodotriisobutylstibine	$(C_4H_9)SbI_2$	70	Friend, 1936, p. 289
Diphenylselenium disulfide	$(C_6H_5)_2SeS_2$	50-51	Friend, 1937, p. 29

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## FACES AND HABITS OF DIAMOND TYPE CRYSTALS

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### ABSTRACT

A study was undertaken of the natural faces and the habits of silicon, germanium, cubic arsenic trioxide and cubic antimony trioxide crystals. The sequence of the crystal forms in their order of appearance was found to be  $\{111\}$ ,  $\{001\}$ ,  $\{113\}$ ,  $\{011\}$ ,  $\{013\}$  for silicon, germanium, and  $\{111\}$ ,  $\{011\}$ ,  $\{001\}$  for cubic arsenic trioxide and cubic antimony trioxide.

### FACES OF THE EQUILIBRIUM FORMS OF DIAMOND TYPE CRYSTALS

#### *Silicon and Germanium*

The investigation of the crystal habits and the study of the natural faces of diamond type crystals reveal valuable facts regarding crystal orientation and surface properties. It is interesting to compare the theoretically expected growth and equilibrium forms with experimental results.

Equilibrium forms of crystals can be obtained by tempering crystals for a long time, at a constant temperature. Where crystals are of macroscopic size, equilibrium may not be reached even after extended tempering. However, by slight periodic alternation of the temperature of the crystal and its surrounding medium (or by very slow crystal growth) faces result which belong to the equilibrium form. These crystals are then said to have tempered, or growth-forms.

Silicon and germanium only, of all the elements with diamond structure, can be prepared in the form of single crystals with natural faces. When permitted to grow rapidly, silicon and germanium crystals display  $\{111\}$  faces only. In particular, silicon crystals grown from the melt and from solutions in gallium, indium<sup>1</sup> and tin, show  $\{111\}$  faces only. This does not confirm the results obtained by D. A. Petrov and A. A. Bukhanova<sup>2</sup> who observed  $\{011\}$  faces only in their study of silicon crystals from tin solution. In Fig. 1 a silicon single crystal, prepared by thermal decomposition of  $\text{SiI}_4$  vapor on a hot silicon substrate, can be seen with  $\{001\}$  and  $\{113\}$  appearing in addition to  $\{111\}$ , and in Fig. 2 another crystal prepared by the same method is shown with  $\{111\}$ ,  $\{001\}$ ,  $\{113\}$ ,  $\{011\}$  and  $\{013\}$ .

Germanium also crystallizes with  $\{111\}$  faces when grown rapidly

<sup>1</sup> Keck, P. H., and Broder, J., *Phys. Rev.*, **90**, 521 (1953).

<sup>2</sup> Petrov, D. A., and Bukhanova, A. A., *Izvest. Akad. Nauk USSR, Otdel. Khim. Nauk*, 396 (1949).

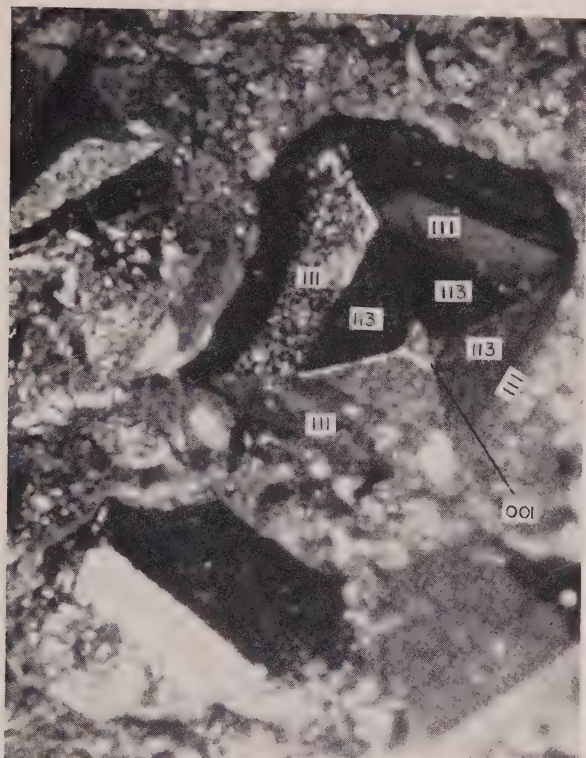


FIG. 1. Silicon crystal\* obtained by thermal decomposition of silicon tetraiodide on a hot silicon substrate showing  $\{111\}$ ,  $\{001\}$  and  $\{113\}$ -planes. All angles are convex ( $72\times$ ).

\* Crystals from Foote Mineral Company, Berwyn, Pa., by the courtesy of Mr. F. B. Litton.

from the vapor. It crystallizes in the same form from the melt,<sup>3</sup> from solutions in gallium and indium, and from the gaseous phase by reduction of germanium tetrachloride with zinc or cadmium vapor. On germanium octahedra grown from the vapor phase, truncated corners were observed which indicate that  $\{001\}$  appears next to the  $\{111\}$  plane. Among tempered germanium crystals, prepared by the hydrogen reduction of germanium tetrachloride,  $\{113\}$  planes were found frequently in addition to  $\{111\}$  and  $\{001\}$ . Finally, on several crystals  $\{011\}$  was also observed (Fig. 3). The results on silicon and germanium crystals are recorded in Table 1.

<sup>3</sup> See also Robinson, S. A., Ostapovich, P. L., Schlegel, E. S., and Gazzara, C. P., *Science*, **116**, 362 (1952).

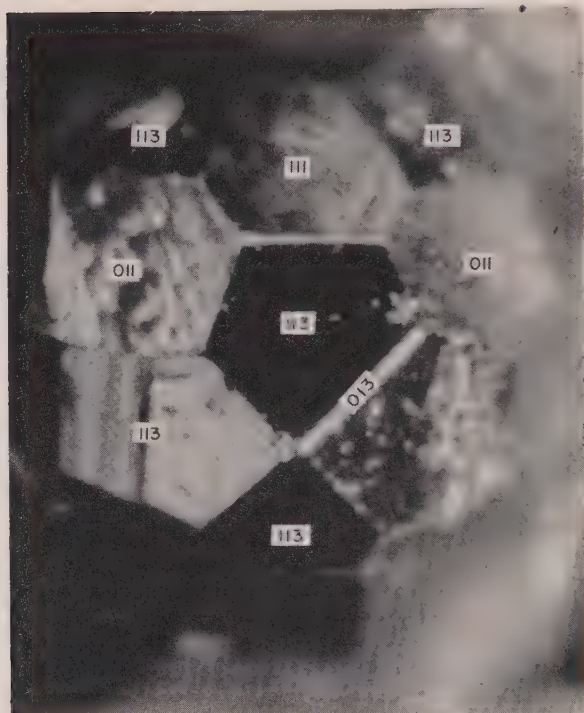


FIG. 2. Silicon crystal\* obtained by thermal decomposition of silicon tetraiodide vapor on a hot silicon substrate showing  $\{111\}$ ,  $\{113\}$ ,  $\{011\}$  and  $\{013\}$ . The  $\{001\}$  plane is poorly developed. One of the  $\{013\}$  planes represented by the truncated edges of adjacent  $\{113\}$  planes is brought out by light reflection. Notice the striation on  $\{113\}$  in  $[1\bar{1}0]$  direction ( $70\times$ ).

\* Crystals from Foote Mineral Company, Berwyn, Pa., by the courtesy of Mr. F. B. Litton.

From these observations, the sequence of the forms in the order of their appearance can be derived as follows:

Silicon:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$ ;  $\{013\}$

Germanium:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$

In the case of silicon, the sequence of the last two forms is not clear. Since  $\{013\}$  was not observed at all in germanium, it may be concluded that the final sequence for the diamond structure is, in general:  $\{111\}$ ;  $\{001\}$ ;  $\{113\}$ ;  $\{011\}$ ;  $\{013\}$ . Figure 4 shows a crystal model exhibiting these planes. This sequence, obtained experimentally, differs slightly from the calculated sequence  $\{111\}$ ,  $\{001\}$ ,  $\{011\}$ ,  $\{113\}$ ,  $\{013\}$ .<sup>4</sup> Details of this subject will be published at a later date.

<sup>4</sup> Stranski, I. N. Discuss. *Faraday Soc.*, **5**, 13 (1949).



TABLE 1. CRYSTALLOGRAPHIC DATA ON SUBSTANCES WITH DIAMOND STRUCTURE

Substance	Planes appearing in growth forms or tempered forms	Preparation method and source of crystals	Twin plane	Slip plane	Cleavage plane
Diamond	{111}*	Geologic formation	{111}	{111} <sup>1</sup>	{111}, {011} <sup>2</sup>
Silicon	{111}	From melt, solutions (SiCl <sub>4</sub> +Zn) gas phase (SiBr <sub>4</sub> +H <sub>2</sub> ) gas phase	{111}	{111} <sup>3</sup>	{111}, {011}
	{111}, {001}	From (SiCl <sub>4</sub> +Zn) gas phase			
	{111}, {001}, {113}	From (SiCl <sub>4</sub> +Zn) gas phase from SiI <sub>4</sub> vapor phase			
	{111}, {001}, {113}, {011}, {013}	From SiI <sub>4</sub> vapor phase			
Germanium	{111}	From vapor, melt, solutions from (GeCl <sub>4</sub> +Zn, Cd) gas phase	{111}	{111} <sup>3</sup>	{111}
	{111}, {001}	From vapor			
	{111}, {001}, {113}	From (GeCl <sub>4</sub> +H <sub>2</sub> ) gas phase			
	{111}, {001}, {113}, {011}	From (GeCl <sub>4</sub> +H <sub>2</sub> ) gas phase			

\* While in diamond a variety of other planes than {111} have been observed, an unambiguous sequence of the appearance cannot be derived because of the complexity of the geological growth conditions.

<sup>1</sup> Tolansky, S., and Omar, M., *Mag.* **44**, 514 (1953).

<sup>2</sup> Kraus, E. H., and Slawson, C. B., *Am. Mineral.*, **24**, 661 (1939).

<sup>3</sup> Trenting, R. G., *J. Metals*, **4**, 1044 (1952).

### Diamond

While the observed sequence should hold true for crystals grown, or tempered, in their vapor phase (or any other highly diluted gaseous mother phase) it may not be valid for diamond crystals. The planes, which appear in addition to the predominant {111} plane in diamond, cannot be arranged distinctly into a sequence, because of the complex conditions during the geological growth.

### Arsenic Trioxide and Antimony Trioxide

A somewhat different sequence of planes is obtained from cubic arsenic trioxide (arsenolite) and cubic antimony trioxide (senarmontite), which are built up of As<sub>4</sub>O<sub>6</sub> and Sb<sub>4</sub>O<sub>6</sub> molecules in the diamond arrangement. These oxides display well developed octahedra, when grown rapidly.

After tempering in the vapor phase, cubic arsenic trioxide and cubic antimony trioxide crystals show {011}, in addition to {111}. In one case, {001} planes were found on arsenic trioxide. Since it is reported in the literature<sup>5</sup> that after tempering {111}, {011} and {001} planes appear on cubic antimony trioxide crystals also, the probable sequence for both cubic arsenic trioxide and cubic antimony trioxide can be given as {111},

<sup>5</sup> Weber, J., *Zeit. Krist.*, **44**, 235 (1908).

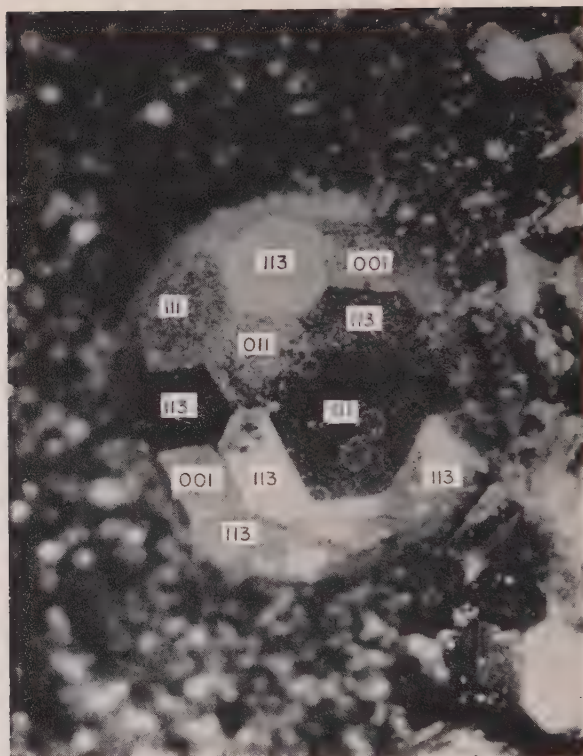


FIG. 3. Germanium crystal\* grown from the gaseous phase by reduction of germanium tetrachloride with hydrogen on a hot graphite block at 900° C. shows {111}, {001}, {113}, and {011} planes (72X).

\* Crystals from the Eagle-Picher Research Laboratories, Joplin, Mo., by the courtesy of Drs. W. E. Medcalf, R. K. Riel and C. E. Smith.

{011}, and {001}. This sequence differs from the sequence for silicon and germanium, and this difference can be explained by the non-spherical symmetry of the molecules ( $T_d$ ). Finally, it might be worthwhile mentioning that cubic basic beryllium acetate, in which the molecules  $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$  occupy the positions of a diamond lattice also crystallizes in the form of octahedra. The results are summarized in Table 2.

#### TWINNING, CLEAVING, SLIPPING AND STRIATION OF DIAMOND TYPE CRYSTALS

Twinning, cleaving and slipping, which are functions mainly of crystal structure, do not depend as much upon growth or tempering conditions as do the crystal habits. Twin planes, cleavage planes and slip planes

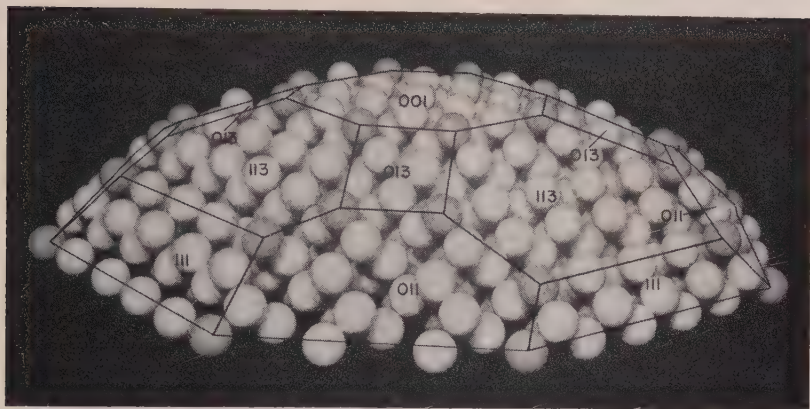


FIG. 4. Model of the supposed equilibrium form of crystals with diamond structure with  $\{111\}$ ,  $\{001\}$ ,  $\{113\}$ ,  $\{011\}$  and  $\{013\}$  planes. The marked balls represent the apexes atoms.

are  $\{111\}$  for silicon and germanium, in all cases. This is also true for diamond crystals. The cleavage planes for cubic arsenic trioxide and cubic antimony trioxide are  $\{111\}$ , however twinning along  $\{111\}$  is not observed. This is in agreement with the theoretical expectation.

In all diamond type crystals striation was found on  $\{111\}$  in the direc-

TABLE 2. CRYSTALLOGRAPHIC DATA ON SUBSTANCES WITH A MOLECULAR LATTICE IN THE DIAMOND ARRANGEMENT

Substance	Planes appearing in growth forms or tempered forms	Preparation method and source of crystals	Twin plane	Cleavage plane
Arsenic trioxide (arsenolite) $\text{As}_4\text{O}_6$	$\{111\}$	From vapor, hydrochloric solution	Not found*	$\{111\}$
	$\{111\}$ , $\{011\}$	From vapor		
	$\{111\}$ , $\{011\}$ , $\{001\}$	From vapor		
Antimony trioxide (senarmontite) $\text{Sb}_4\text{O}_6$	$\{111\}$	From vapor	Not found*	$\{111\}$
	$\{111\}$ , $\{011\}$	From vapor		
	$\{111\}$ , $\{011\}$ , $\{001\}$	From vapor		
Basic beryllium acetate $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$	$\{111\}$	From solutions in organic solvents		

\* As it will be pointed out later  $\{111\}$  twinning in arsenolite and senarmontite is not expected.

tions  $[1\bar{1}0]$ ,  $[10\bar{1}]$ ,  $[01\bar{1}]$ , on  $\{001\}$  in the directions  $[110]$ ,<sup>\*</sup>  $[1\bar{1}0]$ , on  $\{011\}$  and  $\{113\}$ , in the  $[1\bar{1}0]$  direction (Fig. 2). It may be mentioned here that in some cases all major planes in the  $[1\bar{1}0]$  zone between  $\{111\}$  and  $\{001\}$  were found to be developed in silicon crystals grown by the zinc reduction process.

### ZINCBLENDE STRUCTURE

On zincblende structures the general sequence of forms is  $\{111\}$ ,  $\{1\bar{1}1\}$ ,  $\{001\}$ . The zincblende structure may be regarded as a diamond structure with alternating atoms *A* and *B*, having a partial ionic character in addition to the valence bondings. Details will be published at a later date.

### CRYSTAL HABITS

Various types of habits of silicon and germanium crystals from gallium, indium and tin solutions, are formed by cooling. The following habit types were observed: needles with  $[001]$  as needle axis, having the appearance of a string of octahedra along the  $[001]$  axis; twinned and untwinned needles with  $[011]$  as needle axis; plates and rhombus-like plates or rhombohedra. The octahedra appear if there is almost no temperature gradient present during slow cooling; the needles result where there is an appreciable temperature gradient during fast cooling; the plates appear where there is a temperature gradient, near the surface of the solution, resulting from heat losses by radiation. Occasionally, all the types show hollow pits. Dendritic growth was found in silicon plates grown from solution, the growth direction being  $[112]$ . Silicon needles from zinc reduction of silicon tetrachloride in the gaseous phase were found to show almost exclusively the  $[111]$  orientation. They sometimes show interpenetrating twinning. Silicon single crystal fibers (average diameter 1  $\mu$ , length up to 1 cm.) of the same orientation were found by E. R. Johnson and J. A. Amick<sup>6</sup> to occur as cotton wool-like cocoons in the reaction chamber. One batch of silicon crystals prepared by the same process gave a preferred  $[001]$  orientation. These crystals are very similar to the needles obtained from metal solution. Germanium needles prepared by zinc reduction of germanium tetrachloride in the gas phase showed  $[111]$  orientation only.

### ACKNOWLEDGMENT

The author wishes to thank Dr. P. H. Keck for his helpful support and Messrs. J. D. Broder and F. Plock for their assistance in the experimental work.

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<sup>6</sup> Johnson, E. R., and Amick, J. A., *J. Appl. Phys.*, **25**, 1204 (1954).



## TUBULAR MORPHOLOGY OF SOME BRAZILIAN KAOLINS\*

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DE ANDRADE. ELECTRON MICROGRAPHS BY A. C. VILLANOVA

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In the course of some studies on kaolins derived from pegmatites, from Minas Gerais, Brazil, striking differences were observed between these kaolins and those commonly described in the foreign literature, as regards the morphology of the particles. A planar and more or less hexagonal form has generally been ascribed to kaolin particles as revealed by the electron microscope. The Brazilian material, however, shows a completely different morphology, the particles often being of tubular form and having varying opacity and length (Fig. 1).

Initially these tubes were regarded as halloysite, but the frequency of their occurrence in the Brazilian material, compared with the general rarity of halloysite induced the authors to examine the material by  $x$ -rays. Diagrams made with a North American Philips Geiger diffractometer revealed kaolinite and not halloysite (see diagrams and electron micrographs, Figs. 2, 3 and 4).

Numerous samples of Brazilian kaolins from several different sources were examined, together with a few of foreign origin for comparison. The Brazilian samples showed great variation of shape among the particles. The samples from Minas Gerais were collected in places where the kaolin is mined, but those from other localities are probably a few chance specimens from among all that are available at each locality. Samples from the state of São Paulo as a rule show aggregates where great associations of tubular forms are not infrequent. On the other hand, those from the state of Paraná, sedimentary in origin, show large hexagonal plates. Of the samples from the state of Rio, a few show small plates while others show tubes.

The present description is limited mainly to the kaolins from Minas Gerais which display more frequently the tubular morphology and represent deposits over a large area.

Some samples show only tubular particles (Fig. 5) while others show tubes together with ill-shaped flakes (Fig. 6). The tubes when accompanied by flakes of this type present signs of decay which the authors believe usually occurs in three different ways:

(1) By a kind of concentric cleavage so that the tubes are loosened

\* This investigation was first reported to the Brazilian Academy of Science on Aug. 12, 1953, under the title "Morfologia tubular de certos caulins brasileiros."



FIG. 1. Tubular kaolin particles from Minas Gerais, Brazil. Electron micrograph,  $\times 40,000$ . Philips diffractometer trace.

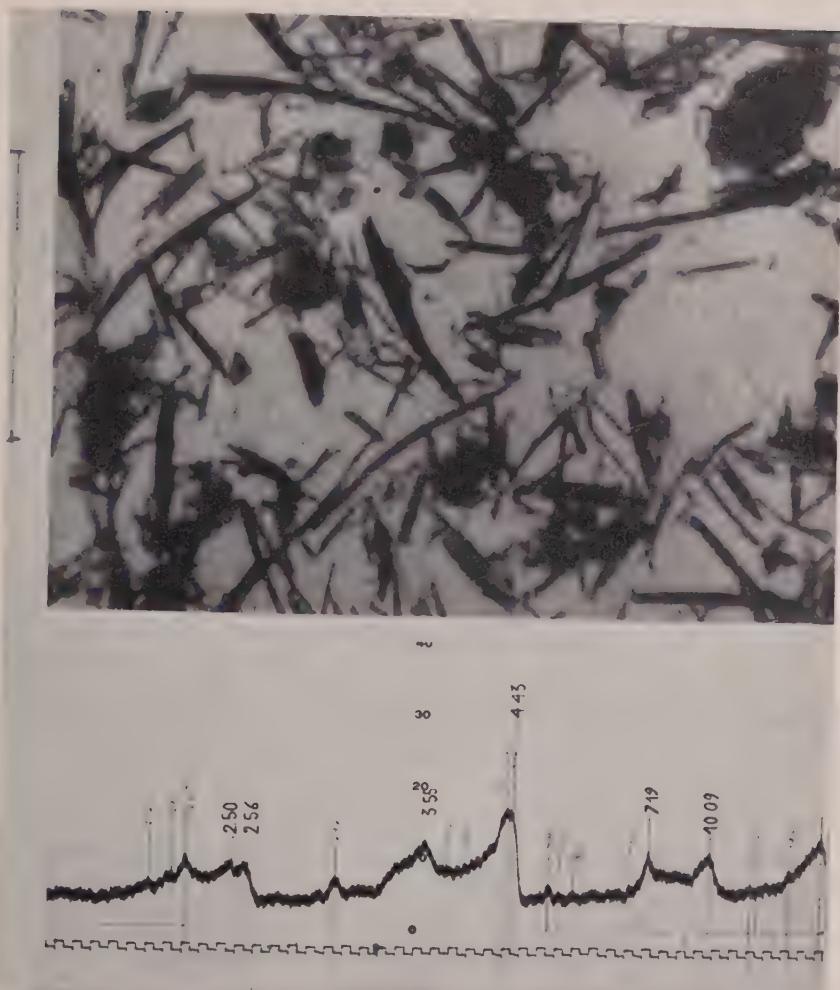


FIG. 2. Tubular halloysite from Djebel-Djebar, Algeria. Electron micrograph,  $\times 40,000$ . Philips diffractometer trace.

and detached from the interior of the tubular formations leaving thinner walls and generating more thin tubes as a result of the cleavage.

(2) By cracking of the tube walls, thus giving rise to the "pill-shaped flakes."

(3) By an indiscriminate breakage of the tubes thereby producing more or less short tubes.

Generally, the three types of deterioration occur at the same time. The concentric cleavage is seen in electron micrographs showing one tube

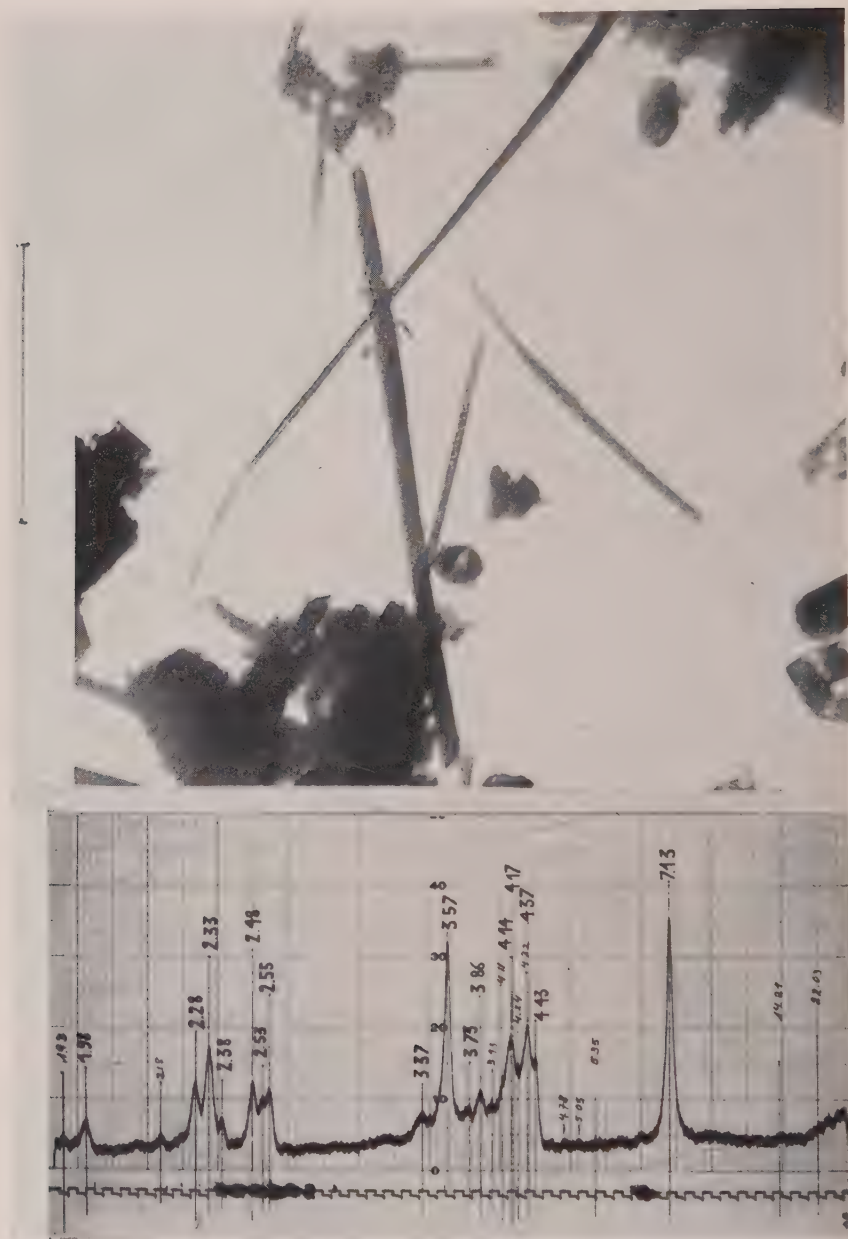


FIG. 3. A kaolinite from Minas Gerais, Brazil. Electron micrograph,  $\times 40,000$ . Philips diffractometer trace.



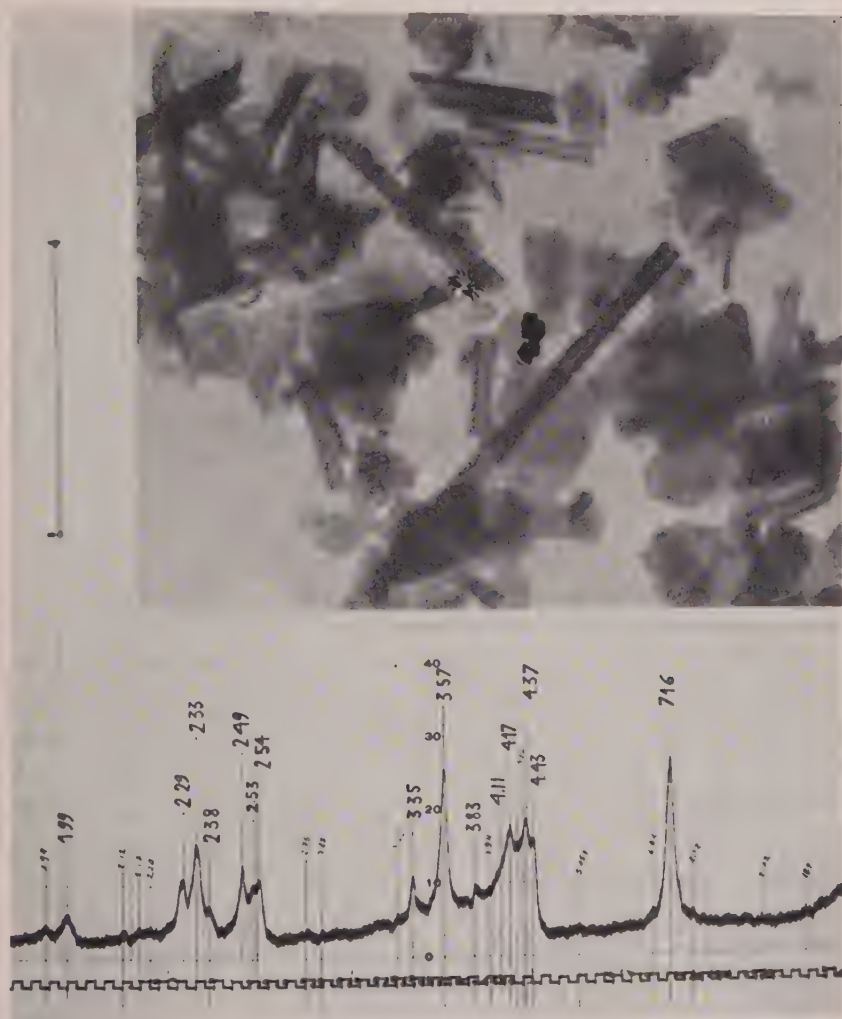


FIG. 4. Kaolinite from Les Eyzies, France. Electron micrograph,  $\times 40,000$  Philips diffractometer trace.

emerging from another; it can be seen in Fig. 3. The destruction of the tubular form by cracking of the walls with the resulting production of ill-shaped particles is visible in Fig. 6 where tubes thick in the center and slender at both ends can be seen next to ill-shaped flakes. In other micrographs, tubes inside other tubes may be observed; in this case, light is noticeable along the walls and not along the central axis of the tube which is dark, meaning that tubes lie within outer tubes.

It is noticeable from the electron micrographs that the tubular formations become emptier and emptier as a result of the concentric cleavage. When the walls of the tubes remain unbroken, the tubes become thinner and thinner, until, when the wall is very thin, the tube may unroll more or less completely and ultimately elongated hexagons are left. The kaolin from Les Eyzies, France (Fig. 4) clearly illustrates this interpretation. Here, tubes and hexagonal, well developed but generally elongated plates are seen. The tubes are not dense nor well rolled, and most of them are almost completely unrolled. All the hexagonal plates seen are shorter than any one of the tubes. These are very long, but by careful observation it is possible to perceive by the degree of transparency that some of

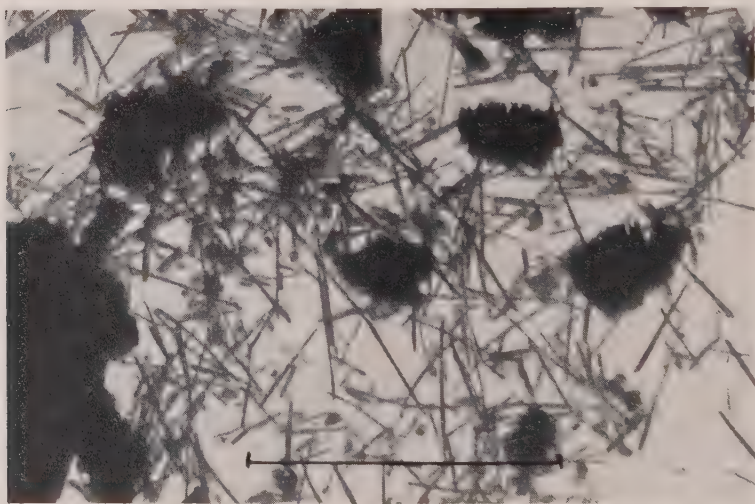


FIG. 5. A sample identified as kaolinite; from Minas Gerais, Brazil,  $\times 7000$ .

them are still attached to others by one of the extremities which means that they have not yet completely detached themselves from the others. When this occurs and when the unrolling has ended, hexagonal plates like those visible in the picture will remain. Apparently, before the tubes are completely unrolled, they have diminished in length, producing plates which are represented by more or less short and large hexagons. It is also possible that due to the cleavage, the elongated hexagons may be divided into many others of smaller size. The elongation of kaolin crystals observed by some authors may be explained in this way; such elongation may be reminiscent of their former tubular shape.

The above observations together with the fact that in sedimentary deposits the occurrence of tubes is non-existent or very rare instead of

frequent as in the residual kaolins from Minas Gerais, suggest an evolutionary process from the tube to the planar hexagonal form. Among the numerous residual and sedimentary samples examined, whenever the particles consisted of hexagonal plates, the percentage of tubes was practically none, but when the tubes predominated, the plates, if any, were ill-shaped.

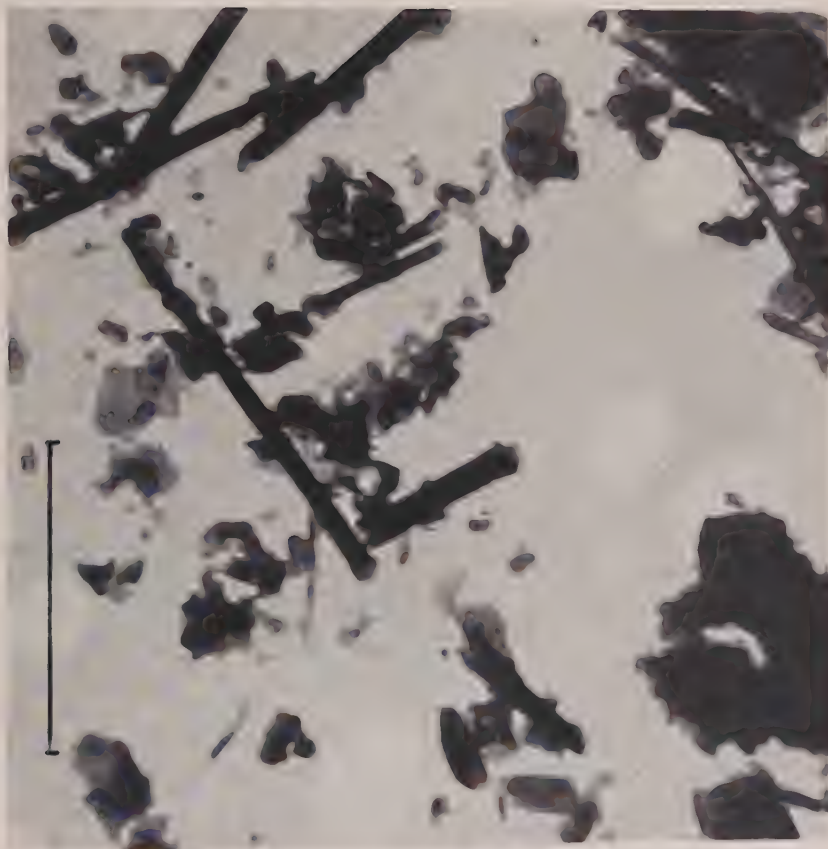


FIG. 6. Tubes next to ill-shaped particles; identified as kaolinite. From Minas Gerais, Brazil.  $\times 40,000$ .

It would be well to mention here that the authors do not think that all residual kaolins display a tubular morphology. The kaolin from St. Austell, England, for example, is of residual origin and shows hexagonal plates in the electron microscope; a hydrothermal action seems to be the principal factor in the genesis of this material. It is possible that, as

in this case, other factors may influence or modify the morphology of the kaolins.

Before examining the samples by the x-ray method, the various morphological types were selected in order to identify them one by one and to verify the existence of possible structural differences between them.



FIG. 7. Vermicular kaolin from Minas Gerais, Brazil. Electron micrograph showing large agglomeration of tubes,  $\times 18,000$ .

Inset shows micrograph taken with phase-contrast microscope,  $\times 600$ .

The results obtained with the Geiger counter diffractometer, together with the electron micrographs, have shown that:

- (1) Material which presented tubes only in the electron microscope was revealed as kaolinite by x-rays.
- (2) Material consisting of hexagonal plates only, gave x-ray diagrams apparently the same as those formerly obtained.



(3) Material consisting of tubes and ill-shaped particles, gave x-ray diagrams analogous to the former ones and also revealed kaolinite.

Furthermore, whenever the tubes are structurally the same as the hexagonal plates, this means that they consist of plates arranged in tubular formations which, when detached according to the natural planes of these formations, will produce hexagonal plates. It is not likely that each tubular formation should be the result of the rolling of a single membrane over itself because this would produce bands instead of peaks in the x-ray diagrams. Furthermore, the coexistence of tubes and plates structurally identified as kaolinite could hardly be explained if the tubes were not made of plates over plates.

The existence of kaolin in tubular form as described above, may help to clarify observations as yet not well explained, especially regarding the "vermicular kaolin." The existence of what is called vermicular kaolin has been mentioned for some time. The authors also have found kaolins of this type as revealed by microscope observation and still more clearly with the phase-contrast microscope (see inset to Fig. 7) but while studying this same material with the electron microscope, it was verified that the so-called vermicular kaolins consisted of large conglomerates or colonies of tubes placed side by side in close and more or less parallel orientation (see electron micrograph in Fig. 7).

An important question regarding the tubular morphology of kaolins, is its influence on the technical properties of this material. In spite of its great purity, the kaolin from Minas Gerais is not considered one of the best when compared with some foreign ones. It is possible that the "particle shape" factor may be partly responsible for its inferior quality as shown by many mechanical tests made by the authors.

The authors wish to take this occasion to express their deep appreciation to Professor G. W. Brindley of the Pennsylvania State University, University Park, Pa., for critically reading, revising and condensing the original manuscript in order to meet the Journal's requirements.

The editor regrets that it has not been possible to reproduce all the electron micrographs submitted by the authors. Certain observations in the paper, such as the large hexagonal flakes frequently shown by kaolinite, and the phenomenon of tubes emerging from tubes, which were well illustrated by the authors, have been frequently illustrated in other publications; these have been omitted for the sake of brevity.

# BASTNAESITE, AN ACCESSORY MINERAL IN THE REDSTONE GRANITE FROM WESTERLY, RHODE ISLAND\*

WILLIAM LEE SMITH AND EVELYN A. CISNEY, *U. S. Geological Survey, Washington 25, D. C.*

## ABSTRACT

Bastnaesite,  $\text{CeFCO}_3$ , has been found in the Redstone granite of Martin (1925), which is one of the granites of the Sterling batholith near Westerly, R. I. It has not previously been recorded as an accessory mineral in granite. X-ray diffraction powder patterns of the bastnaesite compare closely with a pattern obtained from bastnaesite from Mountain Pass, Calif. The three strongest diffraction lines are: 2.88 Å, 3.56 Å, and 1.895 Å. A mean index of refraction measured on fine-grained material is 1.71. Spectrographic analysis showed a major amount of cerium and minor amounts of lanthanum, neodymium, calcium, and fluorine.

## INTRODUCTION

The Redstone granite of Martin (1925) is a phase of the Sterling granite gneiss and is one of the last differentiates of the Sterling batholith. The Sterling batholith, underlying the greater part of the state of Rhode Island and extending into Connecticut and Massachusetts (Hawkins, 1918), is of Pennsylvanian age (Loughlin, 1910). The Redstone granite of Martin (1925) occurs as sheets roughly parallel to the southern margin of the batholith and intrudes the flow-banded Sterling granite gneiss and a metamorphic complex known as the ancient schists. The granites of the Sterling batholith are rich in accessory minerals, several having a high rare-earth content.

In a heavy-mineral study of Martin's Redstone granite, a mineral resembling a finely granular xenotime was found. Martin (1925) mentioned a rare "rust producing" crystal as probably allanite. Kemp (1899) noted these rust blemishes in the Westerly granites spreading from a dark nucleus and staining quartz and feldspar, and he considered the mineral to be altered allanite, adding that it was a poor petrographic subject. Iddings and Cross (1885) described allanite in Westerly granites. Allanite occurs in the monumental granite at Westerly (Quinn, 1943); however, the writers found no allanite in the Redstone granite of Martin (1925). Derby (1891) described monazite in the Redstone granite, and the writers also have noted the presence of monazite. Xenotime is described as present in the Westerly gray granite (Kemp, 1899), however none was found in the Redstone. Young (1938) found keilhauite, a sphene rich in rare earths, in the Sterling granite gneiss. The small

\* Publication authorized by the Director, U. S. Geological Survey.

amount of sphene present in the Redstone granite and in the monumental stone at Westerly (Quinn, 1943) is normal.

Optical, spectrographic, and x-ray analyses clearly establish the "rust producing" mineral in the Redstone granite of Martin (1925) to be bastnaesite, a fluocarbonate of cerium earth minerals. Its occurrence in coarse-grained granite, free of pegmatite or inclusions, and its intimate association with monazite suggest that it is a primary constituent of the rock. Bastnaesite has not previously been described as an accessory mineral in granite other than in contact metamorphic zones or pegmatites.

At Mountain Pass, Calif., bastnaesite occurs in carbonate rock associated with potassium-rich intrusives (Olson et al., 1955). It is present in skarn at Bastnäs, Västmanland, Sweden (Geijer, 1920). It has also been reported in contact zones at Kychtym, Russia (Silberminz, 1929); in the Torendrika-Ifasino region of Madagascar (Koechlin, 1912); and at Jamestown, Colo. (Goddard and Glass, 1940). At Pikes Peak, Colo., bastnaesite is found with tysonite in granite pegmatite (Allen and Comstock, 1880). Glass and Smalley (1945) describe bastnaesite as being present in a brecciated zone near the contact of igneous rock with metamorphosed sediments, in the Gallinas Mountains, New Mexico.

#### SAMPLE LOCATION

At Westerly, R. I., the Redstone granite of Martin (1925) makes up a ridge half a mile wide and two miles long north of Chapman Road. The specimen studied was obtained from the Redstone quarry, shown on the Ashaway (Conn.-R.I.) quadrangle north of the New York, New Haven, and Hartford railroad tracks, half a mile northeast of Westerly. Commercially this granite is known as the "Westerly Red" and should not be confused with the "Westerly monumental granite." The sample collected for study was coarse-grained granite obtained near the center of the body and was free of inclusions and pegmatite.

#### MINERAL SEPARATION

A 10-kg. sample of the granite was crushed to pass a 40-mesh screen. The 80- to 200-mesh fraction of the product of the rolls crusher was separated by means of a hand magnet, bromoform, methylene iodide, and a Frantz isodynamic magnetic separator. Bastnaesite has a specific gravity greater than methylene iodide and separates on the Frantz isodynamic separator between 0.4 and 0.7 amp. at cross and longitudinal settings of 10°. A few grains of bastnaesite remained nonmagnetic up to 1.0 amp. Several grams of bastnaesite were concentrated.

## OPTICAL AND X-RAY EXAMINATION

The bastnaesite occurs in the rock in two forms, as prismatic crystals measuring  $0.05 \times 0.15$  mm. and as irregular aggregates averaging 0.1 mm. in diameter. Both forms are finely granular. The mineral is reddish brown as seen under the petrographic microscope. In immersion liquids an intermediate index of 1.71 can be determined where the coating (probably cerium oxide) has been partly removed by tartaric acid. Dana (Ford, 1932) describes bastnaesite as uniaxal (+),  $\omega = 1.717$ ,  $\epsilon = 1.818$ .

X-ray powder diffraction patterns were made of the concentrates of bastnaesite that separated magnetically on the Frantz isodynamic separator at 0.5, 0.7, and 1.0 amp. These concentrates were mostly the aggregate form of the mineral. In each of the photographs the bastnaesite pattern occurred with a very faint monazite pattern. Monazite had not yet been identified as a component mineral, and it was considered that the monazite and bastnaesite could be intergrown. Monazite subsequently was identified in immersions and separated by hand-picking the sample.

Hand-picked separates of pure bastnaesite of the aggregate variety, magnetic at 0.5 amp., and of the prismatic variety, magnetic at 0.7 amp., were photographed. Both varieties showed bastnaesite powder patterns without the monazite lines. There is no difference between the powder patterns of the prismatic and the aggregate forms of the mineral.

In Table 1 the x-ray powder diffraction pattern of the bastnaesite from the Redstone granite of Martin (1925) is compared with that for bastnaesite from Mountain Pass, Calif. The three strongest diffraction lines of the Redstone granite bastnaesite are 2.88 Å, 3.56 Å, and 1.895 Å. These are in close agreement with the three strongest diffraction lines of the Mountain Pass mineral.

Both the aggregate and prismatic forms of the bastnaesite from the Redstone granite of Martin (1925) are composed of minute crystallites and as a result the patterns produced are faint and diffuse. The measurements were made from the centers of the diffuse lines.

## COMPOSITION OF THE BASTNAESITE

Qualitative spectrographic analysis of the bastnaesite shows cerium to be the only major element. Lanthanum, neodymium, calcium, and fluorine occur as minor components. Aside from detectable contaminants, thorium showed as a minor component. Upon heating the sample, however, the x-ray powder pattern showed the presence of uranoan thioranite; this indicates that thorium is present in other minerals and is not only a substitution for one of the rare earths in the bastnaesite. Chemical



TABLE 1. X-RAY-DIFFRACTION POWDER-PATTERN MEASUREMENTS OF  
BASTNAESITE FROM MOUNTAIN PASS, CALIF., AND WESTERLY, R. I.  
(CuK $\alpha$  RADIATION)

Mountain Pass, Calif. (Film no. 255)		Westerly, R. I. (Film no. 4889)	
$d(\text{\AA})$	$I$	$d(\text{\AA})$	$I$
4.85	M	4.87	W
3.55	S	3.56	S
2.87	S	2.88	M
2.44	F	2.45	VF
2.06	S	2.06	M
2.01	S	2.01	M
1.895	S	1.895	M
1.784	M	1.784	W
1.672	S	1.670	W
1.575	M	1.578	F
1.482	M	1.482	F
1.439	M	1.441	F
1.347	M	1.347	F
1.301	S	1.299	W
1.280	W		VF
1.204	W		VF
1.191	W		VF
1.181	M	1.183	F
1.158	M	1.157	F

The error in measurements is  $\pm 0.05^\circ$ ,  $2\theta$ .

analysis by Alexander Sherwood of the Geological Survey shows the ThO<sub>2</sub> content of the bastnaesite alone to be 0.39 per cent, uranium to be 0.0045 per cent. Phosphorus occurs as a minor constituent and cannot be accounted for by contamination. Phosphorus, however, has a normal affinity for the rare earths as does fluorine (Rankama and Sahama, 1950).

Semiquantitative spectrographic analysis for the trace elements shows yttrium to be present from 0.1 to 0.5 per cent and scandium to be present from 0.01 to 0.05 per cent.

The rare earths are distributed as follows:

>10.	per cent	Ce					
1.-5.	per cent	La	Nd				
0.1-0.5	per cent	Pr	Gd	Sm			
0.01-0.05	per cent	Dy	Er	Eu	Lu	Tb	
0.005-0.01	per cent	Ho	Yb				

Of the Ce-earth metals, Ce>La $\geq$ Nd>Pr $\geq$ Sm>Eu.

Of the Y-earth metals, Gd>Dy $\geq$ Er $\geq$ Lu $\geq$ Tb>Ho>Yb.

This bastnaesite is thus intermediate between the apatite assemblage of Goldschmidt and Thomassen (1924) where  $Ce \geq Nd > Sm \geq Gd \geq Dy \geq Er \geq Yb$ , and the allanite-monzite type (Rankama and Sahama, 1950), which is predominantly Ce earths,  $Ce > Nd > Sm \geq Gd$  but impoverished of the Y earths.

#### PETROGRAPHY

The Redstone granite of Martin (1925) is a coarse-grained red granite. Pink orthoclase feldspar comprises about 45 per cent of the rock. The other major components are approximately: plagioclase 30, smoky quartz 20, and biotite 5 per cent. The plagioclase feldspar was determined by Martin (1925) to be oligoclase with oligoclase-albite rims. Separates were made of the accessory minerals, and the following percentages were estimated for the whole rock:

Magnetite and ilmenite	0.13
Apatite	0.05
Bastnaesite	0.02
Pyrite	0.005
Monazite	0.002
Sphene	0.001
Zircon	0.001
Uranoan thorianite	0.001
Allanite	none
Xenotime	none
Garnet	none

#### ACKNOWLEDGMENTS

We are indebted to Howard Jaffe for suggesting methods of study used in the course of this investigation, to George Hayfield for assistance in the mineral separations, to Daphne D. Riska for assisting in x-ray powder diffraction studies, and to Helen Worthing and Katherine Valentine for spectrographic analyses. This report concerns work done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

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# ABERNATHYITE, A NEW URANIUM MINERAL OF THE METATORBERNITE GROUP\*

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## ABSTRACT

Abernathyite, a new uranium mineral from the Fuemrol No. 2 mine, Emery County, Utah, has the formula  $K(UO_2)(AsO_4) \cdot 4H_2O$ . The mineral occurs as transparent, yellow, fluorescent, thick tabular crystals belonging to the tetragonal system, ditetragonal-dipyramidal class ( $4/m \ 2/m \ 2/m$ ). The space group is  $P4/nmm$ ;  $a_0 = 7.17 \pm 0.01 \text{ \AA}$ ;  $c_0 = 9.08 \pm 0.01 \text{ \AA}$ ;  $a:c = 1:1.266$ ;  $Z = 2$ . Optically, the mineral is uniaxial negative,  $\epsilon = 1.570 \pm 0.003$ ,  $\omega = 1.597 \pm 0.003$ . The hardness is between 2 and 3. The calculated specific gravity is 3.74. The chemical analysis shows, in per cent:  $K_2O$ , 9.5;  $UO_3$ , 57.7;  $As_2O_5$ , 21.6;  $P_2O_5$ , 1.5;  $H_2O -$ , 4.6;  $H_2O +$ , 9.9; total, 104.8. Abernathyite is named for the finder, Jess Abernathy, operator of the Fuemrol mine.

## INTRODUCTION AND ACKNOWLEDGMENTS

In the summer of 1953, Jess Abernathy, operator of the Fuemrol mine, Emery County, Utah, noticed some yellow crystals in his ore. Realizing that they might be of mineralogic importance, he gave the several pieces of sandstone which were coated with crystals to E. B. Gross, mineralogist for the U. S. Atomic Energy Commission in Grand Junction, Colo. Mr. Gross was unable to find in the literature any mineral with corresponding optical properties, and, not having the facilities in Grand Junction for further work, he gave the specimens to A. D. Weeks and M. E. Thompson, mineralogists for the U. S. Geological Survey in Washington, D.C. The study of the mineral was continued in the U. S. Geological Survey, as a part of the Survey's program conducted on behalf of the Raw Materials Division of the U. S. Atomic Energy Commission.

The authors wish to express their appreciation to F. S. Grimaldi, of the U. S. Geological Survey, for his advice and assistance with the problems arising in the course of the chemical analysis. The authors are pleased to name this mineral for the person who found it, Jess Abernathy; without his interest in and appreciation of the mineralogy of his ore, the mineral might have remained undiscovered.

## OCCURRENCE AND ASSOCIATED MINERALS

The Fuemrol No. 2 mine is on a lower slope of Temple Mountain, on the southeast flank of the San Rafael swell, Emery County, Utah, about 47 miles southwest of Green River, Utah (Fig. 1). Mining in the

\* Publication authorized by the Director, U. S. Geological Survey.



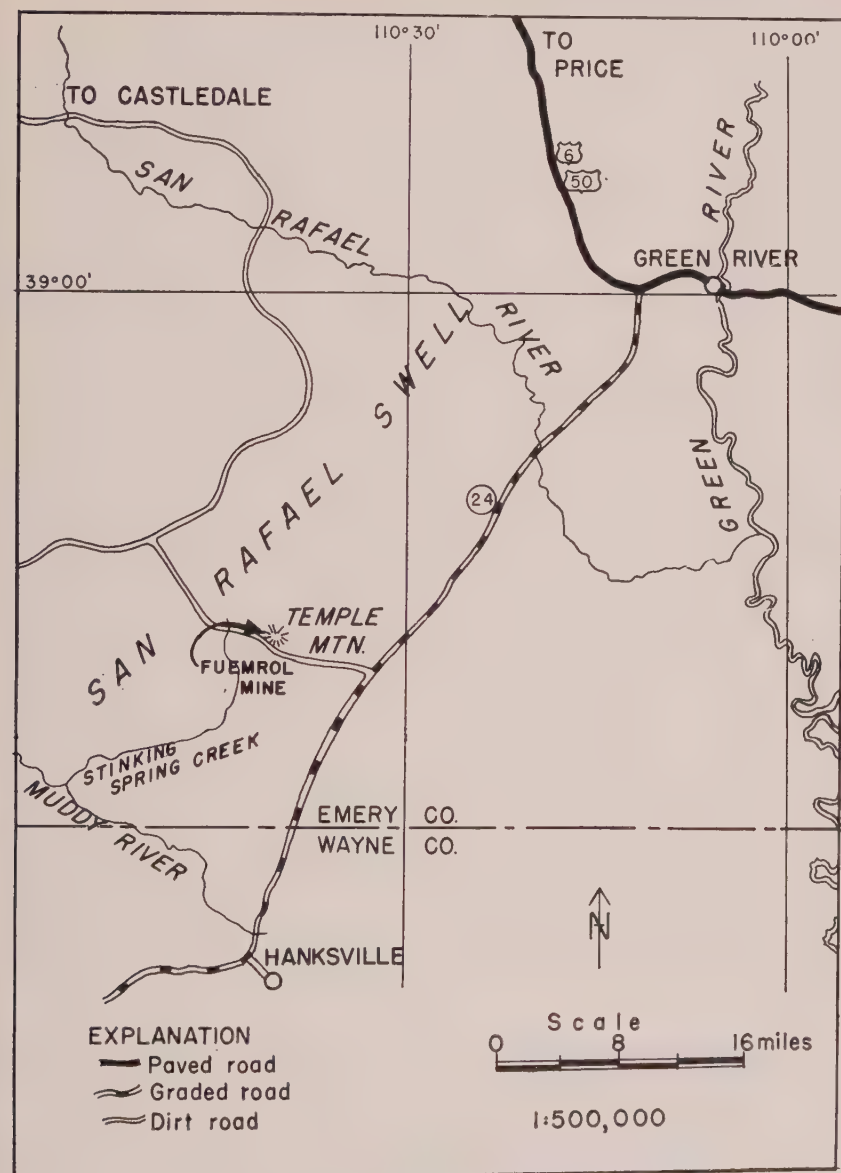


FIG. 1. Index map of locality of abernathyite.

area is in vanadiferous and uraniferous asphaltic sandstones in the Shinarump conglomerate.

Temple Mountain, a small elongate mountain, is capped by Wingate

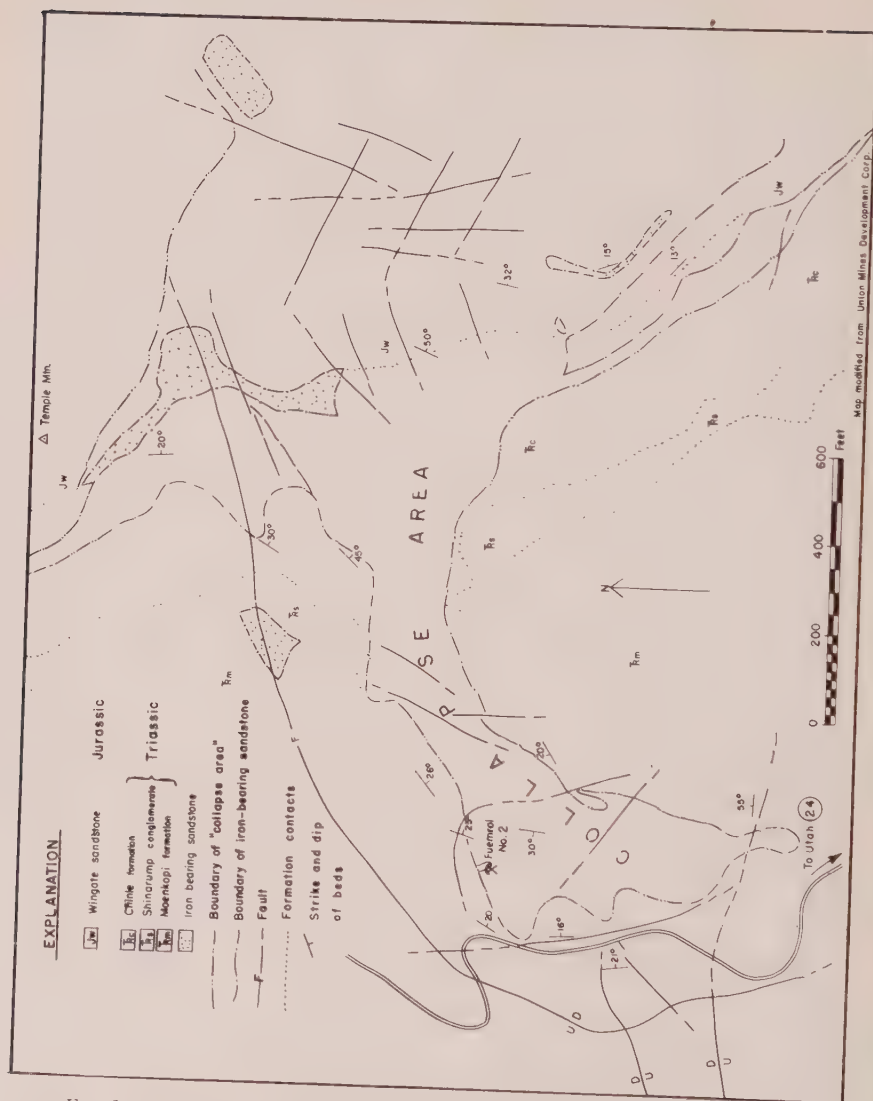


FIG. 2. Geology of the "collapse" area at Temple Mt., Emery County, Utah.

sandstone. Beneath the Wingate sandstone, in descending order, are red sandstones of the Chinle formation, gray Shinarump conglomerate, and red shales and sandstones of the Moenkopi formation. A "collapse" zone (Fig. 2) about 1,800 feet long and 400 feet wide extends below the Wingate sandstone near the central part of the mountain. The area of disturbed rocks has been called the "flop over" or the "tongue."

Within the disturbed area the sandstone has bleached white or gray,

lacks bedding features, and is much fractured. In the upper portions of the flop over, large masses of goethitic and hematitic sandstone are exposed.

At the Fudemrol No. 2 mine near the lower end of the flop over, the sandstone is light to dark gray and contains nodular masses ranging in diameter from 1 to 5 inches. The nodules are composed of sand grains cemented by asphaltite and pyrite. The outer layers of some nodules contain native arsenic, sphalerite, and metazeunerite. The gray to greenish-gray fine-grained sandstone of the Fudemrol mine is composed of poorly sorted subangular grains. Quartz grains make up 65 to 70 per cent of the sandstone; other major constituents are asphaltite and pyrite. Minor constituents are chert, plagioclase, zircon, and muscovite. The cementing material (15 to 20 per cent) is a microcrystalline brownish-gray clay aggregate.

Abernathyite occurs as a crystalline coating lining a fracture in the sandstone and is associated with yellow-brown earthy scorodite. No other minerals were found associated with the new mineral in the samples that were available for this study, but other specimens from the mine contain native arsenic, orpiment, and realgar (T. W. Stern, oral communication). Jarosite, pitticite, metazeunerite, and two other uranyl arsenates of uncertain composition have also been found.

#### PHYSICAL AND OPTICAL PROPERTIES

The crystals of abernathyite are unusually clear and transparent for a mineral of the metatorbernite group. They are yellow, have vitreous luster, and fluoresce moderately a yellow-green color in both long (3660 Å) and short (2537 Å) wavelength ultraviolet light. The streak is pale yellow.

The crystals are thin to thick tabular in habit and occur singly and in groups. Prominent forms are {001} and {110}. They show a perfect basal cleavage, but the cleavage is not micaceous as is typical of other minerals of the metatorbernite group.

The hardness is between 2 and 3. As the largest of the crystals is only about 0.5 mm. on an edge, it was necessary to observe the scratch tests for hardness with a binocular microscope.

An insufficient amount of the mineral was available for a direct measurement of the specific gravity, but the crystals sink in methylene iodide of specific gravity 3.32. The specific gravity is calculated as 3.74 for the pure  $K(UO_2)(AsO_4) \cdot 4H_2O$  compound.

Abernathyite is uniaxial negative,  $\omega = 1.597 \pm 0.003$ , yellow, and  $\epsilon = 1.570 \pm 0.003$ , pale yellow to colorless. A few of the crystals are anomalously biaxial negative, with 2 V less than 5 degrees.

## CHEMICAL ANALYSIS

A qualitative spectrophotographic analysis by K. E. Valentine, of the Geological Survey, showed U, As, P, and K present in amounts more than 1 per cent and trace amounts of Fe, Al, and Si. Only about 25 mg. of material was available for the chemical analysis, and therefore only the principal components as indicated by the spectrophotographic analysis were determined in the chemical analysis. Standard macroanalytical procedures were followed; that is,  $\text{H}_2\text{O}-$  was determined by heating the sample to constant weight at  $110^\circ \text{C}.$ , and  $\text{H}_2\text{O}+$  by heating it to constant weight at  $800^\circ \text{C}.$ ; arsenic was precipitated with  $\text{H}_2\text{S}$  and weighed as  $\text{As}_2\text{S}_5$ ; uranium was determined colorimetrically by the  $\text{NaOH}-\text{H}_2\text{O}_2$  method; potassium was weighed as  $\text{K}_2\text{PtCl}_6$ , and the purity of this precipitate was checked by a spectrophotographic analysis by H. W. Worthing, of the Geological Survey; phosphorus was determined colorimetrically using the molybdenum-blue reaction.

Because questions might be raised about the value of a chemical analysis for which such a small amount of material was available, some of the precautions taken in the analysis are stated here. These precautions consisted mainly of duplicate analyses and of "trial runs" on artificial mixtures. It was possible to make up artificial mixtures containing nearly the correct proportions of As, K, U, and P in advance of the chemical analysis, because the spectrophotographic analysis, the x-ray powder pattern,

TABLE 1. CHEMICAL ANALYSIS OF ABERNATHYITE

Analyst: Blanche Ingram, U. S. Geological Survey

	Analysis of abernathyite	Analysis recalculated to 100 per cent	$\text{K}(\text{UO}_2)(\text{AsO}_4) \cdot 4\text{H}_2\text{O}$
$\text{K}_2\text{O}$	9.5 <sup>1</sup>	9.1	9.0
$\text{UO}_3$	57.7 <sup>2</sup>	55.1	55.0
$\text{As}_2\text{O}_5$	21.6	20.6	22.2
$\text{P}_2\text{O}_5$	1.5	1.4	—
$\text{H}_2\text{O}+$	(9.9)	(9.4)	—
$\text{H}_2\text{O}-$	(4.6)	(4.4)	—
Total $\text{H}_2\text{O}$	14.5 <sup>3</sup>	13.8	13.8
	104.8	100.0	100.0

<sup>1</sup> A value of 8.8 per cent  $\text{K}_2\text{O}$  was obtained in the first analysis. The analysis was then repeated on a larger sample, taking advantage of the information obtained from the first determination. The value of 9.5 per cent  $\text{K}_2\text{O}$  is considered more accurate.

<sup>2</sup> Average of 57.6, 57.6, 57.9.

<sup>3</sup> Average of 14.5, 14.4.



TABLE 2. MOLECULAR RATIOS OF COMPONENTS OF ABERNATHYITE

	Analysis	Molecular weight	Molecular ratios
K <sub>2</sub> O	9.5	94	0.102
UO <sub>3</sub>	57.7	286	0.202
As <sub>2</sub> O <sub>5</sub>	21.6	230	0.094
P <sub>2</sub> O <sub>5</sub>	1.5	142	0.011
H <sub>2</sub> O+	9.9	18	0.550
H <sub>2</sub> O—	4.6	18	0.256

0.105

0.806

and the physical properties of the new mineral made it fairly certain that the mineral was a member of the metatorbernite group and that its formula was probably  $K(UO_2)[(As,P)O_4] \cdot nH_2O$ .

The uranium determination was repeated three times; total H<sub>2</sub>O was determined twice. Potassium was determined gravimetrically twice, the first time on a sample of 5 mg. original weight after H<sub>2</sub>O—, H<sub>2</sub>O+, As<sub>2</sub>O<sub>5</sub>, and UO<sub>3</sub> had been determined. A second analysis for potassium was made by F. S. Grimaldi, of the Geological Survey, on a 10-mg. sample which was treated with HCl and HBr to remove the arsenic. The potassium was then precipitated directly. These repeat analyses gave consistent results.

The results of the chemical analysis total 104.8 per cent. No explanation for this high total is offered. The analysis, when recalculated to 100 per cent, agrees very closely with the theoretical composition (Table 1).

The molecular ratios obtained from the analysis are very close to ideal proportions (Table 2). The simplest formula to be obtained from these ratios is  $K(UO_2)(AsO_4) \cdot 4H_2O$ . A small amount of phosphorus substitutes for arsenic in the ratio of one part P<sub>2</sub>O<sub>5</sub> to 14.4 parts As<sub>2</sub>O<sub>5</sub> by weight.

#### X-RAY DATA

An x-ray diffraction powder pattern was taken by D. D. Riska, of the Geological Survey, with a Debye-Scherrer camera (114.59-mm. diameter) using Ni-filtered Cu radiation. The pattern of abernathyite very closely resembles the patterns of several other members of the metatorbernite group—synthetic hydrogen-autunite, metatorbernite, and metazeunerite. The pattern was easily indexed by comparing it with a pattern of another member of the group whose cell dimensions were known (Table 3).

The cell dimensions of abernathyite and several other minerals and artificial compounds that are generally considered to belong to the meta-

TABLE 3. X-RAY DIFFRACTION POWDER DATA AND UNIT-CELL  
CONSTANTS OF ABERNATHYITE

Space group:  $P4/nmm$ ;  $a_0 = 7.17 \pm 0.01 \text{ \AA}$ ;  $c_0 = 9.08 \pm 0.01 \text{ \AA}$ ;  
 $a_0 : c_0 = 1 : 1.266$ ;  $Z = 2$

<i>I</i>	$d_{(\text{meas})}$	$d_{(\text{calc})}$	<i>hkl</i>
10, broad	9.14	9.08	001
7	5.63	5.63	101
4	5.11	5.07	110
4	4.58	4.54	002
4	4.43	4.43	111
8, broad	3.84	3.84	102
7	3.59	3.59	200
8	3.34	{ 3.38 3.34	{ 112 201
1	3.16		
5	3.02	{ 3.03 3.02	{ 003 211
6, broad	2.79	{ 2.81 2.79	{ 202 103
5, broad	2.61	{ 2.63 2.62	{ 113 212
3	2.54	2.54	220
5	2.45	2.44	221
3	2.32	{ 2.31 2.31	{ 203 301
6	2.28	{ 2.27 2.27	{ 004 310
		2.21	222
6	2.21	{ 2.21 2.20	{ 213 311
2	2.17	2.16	104
6	2.12	2.12	302
6	2.07	2.07	114
		2.03	312
3	1.948	{ 1.943 1.943	{ 321 223
1	1.919	1.918	204
3	1.879	1.876	303
1	1.855	1.853	214
5	1.822	{ 1.822 1.816 1.815	{ 322 005 313
3	1.797	1.793	400
3	1.780	1.760	104
		1.759	401
6	1.712	{ 1.710 1.710	{ 411 115

TABLE 3—(continued)

<i>I</i>	<i>d</i> <sub>(meas)</sub>	<i>d</i> <sub>(calc)</sub>	<i>hkl</i>
3	1.667	1.691	224
		{ 1.667	402
		{ 1.667	330
		1.662	331
		1.662	323
		1.646	304
		1.641	420
3	1.625	1.624	412
		1.620	205
6	1.606		
3	1.582	{ 1.584	332
		{ 1.580	215
		{ 1.579	421
		1.542	403
3	1.514	1.512	422
		1.508	413
3	1.482		
3	1.458		
6	1.421		
3	1.372		
1	1.359		
1	1.300		
5	1.280		
4	1.261		
1, broad	1.240		
1, broad	1.212		
3	1.206		
3	1.198		
1	1.187		

torbernite group are listed in Table 4 for comparison. We are grateful to Gabrielle Donnay, of the Geological Survey, for the measurement of the

TABLE 4. COMPARISON OF UNIT-CELL DIMENSIONS OF ABERNATHYITE WITH THOSE OF OTHER MEMBERS OF THE METATORBERNITE GROUP

Mineral or compound	<i>a</i> <sub>0</sub> (Å)	<i>c</i> <sub>0</sub> (Å)	Reference
Abernathyite K(UO <sub>2</sub> )(AsO <sub>4</sub> ) · 4H <sub>2</sub> O	7.17	9.08	— <sup>2</sup>
Synthetic troegerite H(UO <sub>2</sub> )(AsO <sub>4</sub> ) · 4H <sub>2</sub> O	7.16	8.80	— <sup>1</sup>
Synthetic Na(UO <sub>2</sub> )(AsO <sub>4</sub> ) · 4H <sub>2</sub> O	7.12	8.70	— <sup>1</sup>
Synthetic NH <sub>4</sub> (UO <sub>2</sub> )(AsO <sub>4</sub> ) · 4H <sub>2</sub> O	7.21	8.85	— <sup>1</sup>
Meta-autunite I Ca(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> · 2½–6½H <sub>2</sub> O	6.98	8.42	— <sup>2</sup>
Metatorbernite Cu(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> · 8H <sub>2</sub> O	6.95	2 × 8.70	— <sup>2</sup>

<sup>1</sup> Mrose, M. E., 1953.<sup>2</sup> Donnay, Gabrielle (oral communication).

lattice constants of abernathyite from Buerger precession photographs. The constants are given as follows:  $a_0 = 7.17 \pm 0.01 \text{ \AA}$ ;  $c_0 = 9.08 \pm 0.01 \text{ \AA}$ ; space group  $P4/nmm$  ( $D_4^7h$ ); cell contents 2 formula units  $K(UO_2)(AsO_4) \cdot 4H_2O$ . The calculated density is 3.74.

Beintema (1938) assigned meta-autunite to the space group  $P4/nmm$ , but he had to postulate a statistical distribution of Ca over half the symmetrically equivalent sites in the crystal structure in order to account for this high symmetry. Recently, G. Donnay (oral communication) found that this mineral and others in the group actually have lower symmetries as well as true cells which are multiples of Beintema's cell, so that the cations are in reality in ordered arrangement. On the other hand, her measurements indicate that the true symmetry of abernathyite is  $P4/nmm$  with all the cation sites occupied by K ions, of which there are twice as many as there are Ca ions in meta-autunite.

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## ALLEVARDITE, A SWELLING DOUBLE-LAYER MICA MINERAL\*

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### ABSTRACT

The structure contains pairs of mica-like layers linked by 0.7 (K, Ca) ions/unit cell. These pairs of layers are separated by 0, 1, 2 or 3 layers of water molecules each containing 2 molecules/unit cell. One-dimensional fourier syntheses of electron density reveal the number and position of the interlayer cations and water molecules. Comparison with vermiculite shows significant differences. At high temperatures, around 900° C., the loss of (OH) groups without disruption of the layer structure is demonstrated. Organic complexes of allevardite are compared with those of montmorillonite. A fourier synthesis of the ethylene glycol complex suggests the orientation of the organic molecules between the silicate layers.

### INTRODUCTION

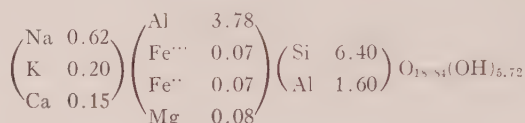
This mineral, from a locality near Allevard, France, has a remarkable skin-like appearance. When first studied (Caillère 1934, 1936; Lemoine 1935; Déribéré, 1943) there was considerable dispute as to its true character but Caillère, Mathieu-Sicaud and Hénin (1950) showed it was a mica-type mineral with layers of water molecules separating double mica-like layers. A specimen of this mineral, presented to the writer by Mlle. Caillère, when examined by an x-ray diffractometer gave a long series of basal reflections, from which fourier syntheses of electron-density have been derived. The alumino-silicate layers have been shown to be essentially the same as in the muscovite structure, so that in calculating the signs of the structure factors used in the fourier syntheses, the silicate layer has played the same role as a heavy atom by dominating the phases of the reflections. The crystallization of the mineral is too imperfect for more general reflections to be studied so that two-dimensional syntheses have not been possible.

### CHEMICAL COMPOSITION AND STRUCTURAL FORMULA

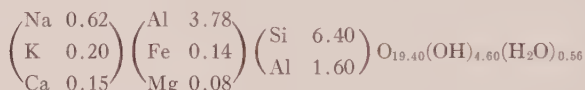
A structural formula has been evaluated from the latest chemical analysis of allevardite (see Table 1) by Hénin, Esquevin and Caillère (1954) by assuming 12 ions of Si, Al, Fe, Mg in tetrahedral and octahedral positions, as in muscovite. Small percentages of TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> have been neglected without assigning them to any particular mineral impurity, and the H<sub>2</sub>O+ content has been taken as 6.04% as given by Caillère *et al.* (1950) which is consistent with the later analysis (see

\* Contribution No. 54-23 from the College of Mineral Industries, The Pennsylvania State University.

Table 1). The formula thus obtained is:



The excess of (O+OH) over the 24 available sites in the layers is attributed to interlayer water and the formula can be re-written:



Hénin *et al.* (1954), recognizing the uncertainty of the H<sub>2</sub>O determination, evaluated a formula on the basis of O=11, which is equivalent to assuming a mica composition with exactly O<sub>10</sub>(OH)<sub>2</sub>, (this is numerically equivalent to O<sub>11</sub>+H<sub>2</sub>O). It is also tantamount to assuming a total negative charge, and therefore also a total positive charge, of 22 units for which there is no real justification.

TABLE 1. CHEMICAL ANALYSIS OF ALLEVARDITE

(After Hénin, Esquevin & Caillère, 1954)

SiO <sub>2</sub>	45.20	MgO	0.35
Al <sub>2</sub> O <sub>3</sub>	32.15	K <sub>2</sub> O	1.10
Fe <sub>2</sub> O <sub>3</sub>	0.65	Na <sub>2</sub> O	2.25
FeO	0.55	P <sub>2</sub> O <sub>5</sub>	0.15
TiO <sub>2</sub>	0.30	H <sub>2</sub> O	15.80
CaO	1.00		
		Total	59.50

(After Caillère, Hénin & Mathieu-Sicaud (1950)

H <sub>2</sub> O—	9.72	H <sub>2</sub> O Total	15.76
H <sub>2</sub> O+	6.04		

### THE BASAL REFLECTIONS

The spacings and intensities have been measured using Geiger counter diffractometers (General Electric XRD3 and Philips wide range instruments). Integrated intensities have been measured from specimens consisting of thin flat rectangular sheets ranging in area from about 5 × 10 mm. to 10 × 15 mm. and of thickness about 0.1 mm., by (a) taking counts/second at suitably spaced angular intervals and integrating graphically, (b) direct chart recording and graphical integration. The

mineral occurs in a skin-like form with a high degree of orientation of the basal (001) planes, and it has been assumed that reflection from a flake is equivalent to reflection by an extended surface of a mosaic crystal.

#### LATTICE SPACINGS OF NATURAL, HYDRATED AND HEAT-TREATED ALLEVARDITE

The basal spacings of allevardite after various treatments are recorded in Table 2. Four distinct hydration states are clearly recognized corresponding to zero, one, two and three layers of water molecules be-

TABLE 2. LATTICE SPACINGS,  $d(001)$ , OF HYDRATED AND HEAT-TREATED SPECIMENS OF ALLEVARDITE

$$\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$$

Condition of Mineral	$d(001)$ , $\text{\AA}$	Number of water layers per unit cell
Immersed in water	$28.36 \pm 0.05$	3
Air-dry, natural state	$24.62 \pm 0.05$	2
Immediately after heating to $110^\circ\text{--}120^\circ \text{C}$ .	$c \ 21.5$	1
Air-dry, after treatment with 1:10 HCl	$22.00 \pm 0.05$	1
After 24 hr. at $450^\circ \text{C}$ .	$19.09 \pm 0.02$	0
After 24 hr. at $560^\circ \text{C}$ .	$19.24 \pm 0.04$	0
After 24 hr. at $650^\circ \text{C}$ .	$19.28 \pm 0.04$	0
After 24 hr. at $760^\circ \text{C}$ .	$19.33 \pm 0.03$	0
After 24 hr. at $900^\circ \text{C}$ .	$19.38 \pm 0.01$	0
After 24 hr. at $1000^\circ \text{C}$ .	decomposed	0

tween the silicate layers. Twenty or more orders of reflection are recorded, showing that the sequence of layers is highly regular and suitable for detailed study by fourier synthesis.

The mineral is irreversibly dehydrated when heated to about  $450^\circ \text{C}$ . From  $450^\circ \text{C}$ . to  $900^\circ \text{C}$ . there is a small but consistent increase of  $d(001)$  which is not a thermal expansion effect, since all measurements were made after cooling the specimen to room temperature. The mineral decomposes at  $1000^\circ \text{C}$ ., the principal product being mullite, with some cristobalite.

#### FOURIER SYNTHESIS OF ELECTRON DENSITY NORMAL TO THE BASAL PLANE

Structure factors were derived from the integrated intensities by correcting for Lorentz and polarization factors and using the expression ap-

propriate to x-ray reflection by an extended mosaic crystal. Their signs were determined by assuming the structure consists of pairs of mica-type layers bound together by some or all of the cations K, Na and Ca, and with water layers separating pairs of bound mica layers. The best layer parameters were then determined by difference syntheses.

TABLE 3. X-RAY DATA FOR ALLEVARDITE (HEAT-TREATED SPECIMENS)

$$\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$$

<i>l</i>	560° C., 24 hr.				900° C., 24 hr.		
	<i>d</i> (00 <i>l</i> ) Å	<i>d</i> (001) Å	<i>F</i>   <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>d</i> (00 <i>l</i> ) Å	<i>d</i> (001) Å	<i>F</i>   <sub>obs</sub>
1	19.2	19.2*	6.1	3.6	19.4	19.4*	5.6
2	9.61	19.22*	25.9	-19.7	9.72	19.44*	16.2
3	6.417	19.25	8.2	3.5	6.487	19.46*	8.2
4	4.809	19.24	30.2	-22.7	4.848	19.39	29.4
5	3.850	19.25	6.6	3.2	3.883	19.41	5.9
6	3.186	19.12	59.4	-50.8	3.232	19.39	67.9
7	—	—	—	2.9	—	—	—
8	2.418	19.34	5.0	-9.7	2.423	19.38	11.0
9	—	—	—	2.6	—	—	—
10	1.918	19.18	43.9	39.4	1.937	19.37	36.8
11	—	—	—	2.3	—	—	—
12	1.607	19.28	16.8	10.3	1.614	19.37	23.2
13	—	—	—	2.0	—	—	—
14	1.377	19.28	26.9	-26.7	1.386	19.40	32.0
15	—	—	—	1.8	—	—	—
16	1.202	19.23	16.5	30.5	1.211	19.38	17.3
17	—	—	—	1.7	—	—	—
18	—	—	—	-5.4	—	—	—
19	—	—	—	1.5	—	—	—
20	0.9621	19.24	16.7	12.5	0.9691	19.38	12.5
21	—	—	—	1.3	—	—	—
22	0.8745	19.24	18.2	-26.5	0.8810	19.38	14.2

Mean *d*(001) 19.24±0.04Mean *d*(001) 19.38±0.01

\* Values not incorporated in the average value.

*F* values correspond to one-quarter of the unit cell content.(a) *Allevardite after heat-treatment at 560° C.*

Caillière *et al.* (1950) stated that a specimen heated to 550° C. gave an x-ray pattern similar to that of ground muscovite. This is incorrect; they probably failed to observe the weak odd-order reflections, the first three of which are easily measurable with a counter diffractometer. Table 3 lists the basal spacings, and the observed and calculated struc-



ture factors. The layer parameters used in calculating the scattering factors are listed in Table 5. Figure 1 shows the electron density distributions derived from the observed and calculated scattering factors.

The close agreement between the observed and calculated data (structure factors and electron density curves) enables us to discuss the situation existing at  $z=0$  and  $z=9.62 \text{ \AA}$  (i.e.,  $c/2$ ), where interlayer bonding cations would be expected to occur. The small peak at  $z=0$

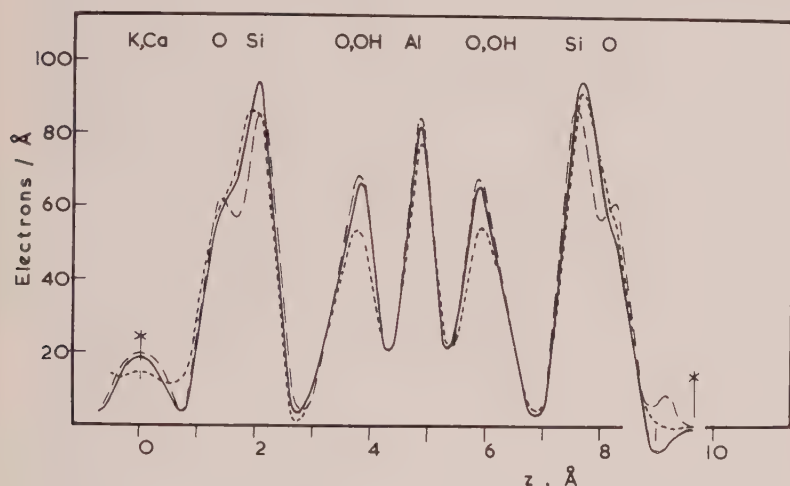


FIG. 1. Electron density distributions in allevardite: full line ——— derived from experimental structure factors after heat-treatment at  $560^\circ \text{C}$ . to remove water layers, dashed line — — — derived from calculated structure factors, dotted line ····· derived from experimental structure factors after heat-treatment at  $900^\circ \text{C}$ .; observe the diminution of the OH peaks. Symmetry centers for the one-dimensional distribution marked \*.

corresponds to about 14 electrons per unit cell. It can be compared with the chemical analysis if the formula is written as follows:

$$\begin{pmatrix} \text{Na} & 1.26 \\ \text{K} & 0.40 \\ \text{Ca} & 0.30 \end{pmatrix} \left[ \begin{pmatrix} \text{Al} & 3.78 \\ \text{Fe} & 0.14 \\ \text{Mg} & 0.08 \end{pmatrix} \begin{pmatrix} \text{Si} & 6.40 \\ \text{Al} & 1.60 \end{pmatrix} \begin{pmatrix} \text{O}_{19.40} \\ \text{OH}_{4.60} \end{pmatrix} \right]_2$$

where the large bracket taken twice represents the two layers in the unit cell and the ions Na, K and Ca are available for bonding the layers together. They provide, however, a total of  $12+7+5=24$  electrons, which is far in excess of the electron peak at  $z=0$ . The most probable explanation is that some of the cations Na, K, Ca are present as impurities and/or are adsorbed to the external surfaces of the mineral. X-rays cannot determine which of these cations are in the structure, but since

sodium micas are rare, it seems most likely that the layers are bound by the (K+Ca) ions which together furnish about the right number of electrons.

The absence of a peak at  $c/2$ , which is confirmed by the subsequent fourier syntheses, shows that the cations not accommodated at  $z=0$  do not occur at  $z=c/2$ . All the evidence points to an absence of cations at this level.

(b) *Allevardite after heat-treatment at 900° C.*

Lattice spacings and structure factors are tabulated in Table 3 and the electron distribution is shown by the dotted line in Fig. 1. The main

TABLE 4. X-RAY DATA FOR ALLEVDARITE (AIR-DRY, UNTREATED MINERAL)

$$\lambda(\text{CuK}\alpha)=1.5418 \text{ \AA}$$

$l$	$d(00l)$ Å	$d(001)$ Å	$ F _{\text{obs}}$	$F_{\text{calc}}$
1	24.21	24.21*	45.4	45.5
2	12.28	24.56*	41.4	-43.8
3	8.27	24.81*	3.7	-13.8
4	6.16	24.64	4.7	-1.3
5	4.941	24.70	36.0	-29.0
6	4.086	24.52	tr.	1.0
7	3.520	24.64	19.7	-17.2
8	3.089	24.71	65.4	-57.6
9	2.722	24.50	6.4	5.5
10	—	—	0.	1.4
11	2.240	24.64	14.1	-13.2
12	2.053	24.64	23.6	17.2
13	1.899	24.69	38.8	41.8
14	1.768	24.75	9.0	9.2
15	—	—	0.	-1.4
16	1.542	24.67	16.2	16.9
17	1.446	24.58	5.4	-5.1
18	1.370	24.66	18.0	-23.9
19	1.301	24.72	9.6	-7.2
20	1.234	24.68	11.3	16.2
21	1.175	24.67	11.0	11.9
26	0.9469	24.62		

Mean  $d(001)$   $24.65 \pm .05$

Other values  $\begin{cases} 24.62 \pm .02 \\ 24.58 \pm .05 \end{cases}$

Overall mean value:  $24.62 \pm 0.05$

\* Values not incorporated in the average value.

$F$  values correspond to one-quarter of the unit-cell content.

effect of heating at the higher temperature is a diminution of the peaks associated with  $(4\text{ O} + 2\text{ OH})$ , which can be attributed to dehydroxylation. If  $4\text{ O} + 2(\text{OH})$  becomes  $5\text{ O} + \text{H}_2\text{O}$ , a diminution of the O, OH peak by one-sixth of its electron content would be expected and this is consistent with the fourier synthesis. Muscovite mica has recently been studied by the writer and Mr. Vanden Heuvel in a similar way and similar results have been obtained.

(c) *Allevardite under normal air-dry conditions, without heat-treatment.*

The basal spacings and structure factors are listed in Table 4. The parameters for the atomic layers and the number of  $\text{H}_2\text{O}$  molecules per layer were determined by repeated fourier syntheses; the final parameters are given in Table 5, and the fourier syntheses in Fig. 2. The analysis shows about 12 electrons/unit cell at  $z=0$  (thus confirming the result obtained with the  $560^\circ\text{ C.}$  heated material), 2  $\text{H}_2\text{O}$  molecules per unit cell at  $z=10.85\text{ \AA}$  and an absence of atoms at  $z=c/2$  ( $12.31\text{ \AA}$ ). The slightly poorer resolution of the peaks in Fig. 2 than in Fig. 1, arises from the fact that the highest order reflection used for the air-dry natural mineral, the 21st order, has a  $d$ -value of  $1.175\text{ \AA}$  whereas for the  $560^\circ\text{ C.}$  heated material a 22nd order was used with a  $d$ -value of  $0.874\text{ \AA}$ .

(d) *Allevardite in other states of hydration.*

Allevardite after 1:10 HCl treatment, with one layer of water molecules between the silicate layers, was examined by fourier synthesis and the results confirm the presence of cations containing about 12.15 electrons/unit cell between the silicate layers and one water layer at

TABLE 5.  $z$  PARAMETERS OF ATOMIC LAYERS IN ALLEVARDITE, IN  $\text{\AA}$

Natural air-dry material		Mineral heated to $560^\circ\text{ C.}$		Ethylene glycol allevardite	
$z=c/2^*$	12.31	$z=c/2^*$	9.62	$z=c/2^*$	13.24
2 $\text{H}_2\text{O}$	10.85			$1\frac{1}{2}\text{ CH}_2\text{OH}$	12.06
6 O	8.02			$1\frac{1}{2}\text{ CH}_2\text{OH}$	11.03
4 Si, Al	7.42	6 O	8.13	6 O	7.96
6 O, OH	5.83	4 Si, Al	7.48	4 Si, Al	7.37
4 Al	4.76	6 O, OH	5.88	6 O, OH	5.75
6 O, OH	3.69	4 Al	4.81	4 Al	4.75
4 Si, Al	2.10	6 O, OH	3.74	6 O, OH	3.75
6 O	1.50	4 Si, Al	2.14	4 Si, Al	2.13
0.7 K, Ca*	0	6 O	1.49	6 O	1.54
		0.7 K, Ca*	0	0.7 K, Ca*	0

\* Indicates a symmetry centre for the layer sequence.

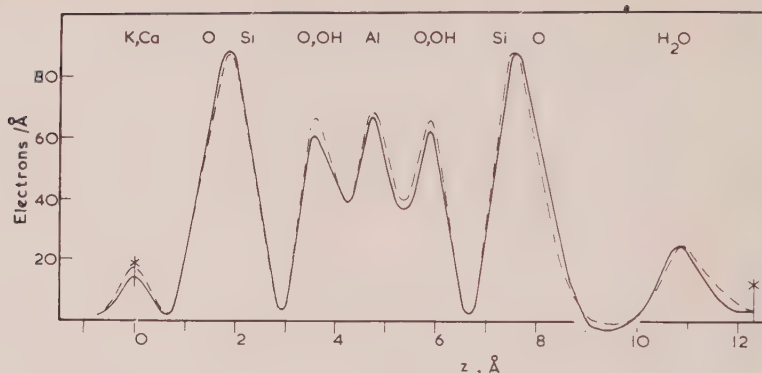


FIG. 2. Electron density distribution in natural air-dry alleverdite; full line based on experimental structure factors, dashed line on calculated structure factors. Symmetry centers marked \*. Note that the water layer is duplicated by the symmetry center at  $z=12.31$  Å.

$z=c/2$  containing 2 water molecules/unit cell. Water wet flakes containing three water layers between the silicate layers were not suitable for accurate intensity measurements and fourier synthesis was not attempted.

#### DISCUSSION OF THE HYDRATION STATES OF ALLEVERDITE; COMPARISON WITH VERMICULITE

Figure 3, (a), (b), (c) and (d), represents diagrammatically the distribution of water layers in the four hydration states. In case (a), fourier

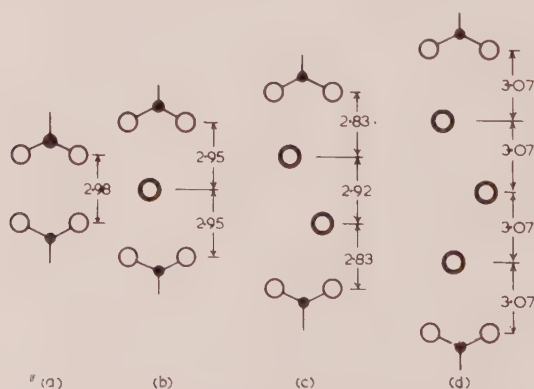


FIG. 3. Diagrammatic representation of the four hydration stages of alleverdite. Heavy circles represent layers of water molecules, light circle oxygen atoms and small black circles silicon atoms.



synthesis has shown that the interlayer space at  $z=c/2$  occupies 2.98 Å between centers of oxygen atoms. In case (b), if the silicate layer (about 16.1 Å thick) is subtracted from  $d(001)=22.00$  Å, the interlayer space is 5.9 Å wide and the oxygen-water separation is 2.95 Å. In case (c), fourier synthesis has given the layer separations,  $O-H_2O=2.83$  Å,  $H_2O-H_2O=2.92$  Å. In case (d), we obtain after subtracting 16.1 Å from  $d(001)$ , 28.38 Å, a value 12.3 Å, i.e., 3.07 Å for the average  $O-H_2O$  and  $H_2O-H_2O$  layer separations. These separations lie within  $\pm 0.1$  Å of an average value 2.95 Å.

Comparison can be made with the results obtained for the interlayer region of vermiculite by Mathieson and Walker (1954) and independently by Grudemo (1954). Vermiculite normally contains two water layers between aluminosilicate layers, and the exchangeable cations (mainly Mg in the naturally occurring mineral) lie between the water layers. Mathieson and Walker give the following layer separations,  $O-H_2O=2.84$  and  $H_2O-H_2O=2.14$ . Grudemo obtains similar results. The  $O-H_2O$  separation is about the same in vermiculite as in allevardite, but the  $H_2O-H_2O$  layer separation is considerably less in vermiculite due to the presence of cations between the water layers. The near equality of the  $O-H_2O$  and  $H_2O-H_2O$  separations in allevardite is consistent with an absence of cations between the water layers, as shown by the fourier syntheses. The layer density of water molecules in vermiculite is about 4.3  $H_2O$  per layer as compared with only 2  $H_2O$  per layer in allevardite.

Comparison can also be made with the weight-loss measurements made by Caillère *et al.* (1950). The smaller inflections in their weight-loss versus temperature curve have no obvious structural significance, but the main 'plateaux' can be correlated with the loss of interlayer water and of hydroxyl radicals. From 200°–500° C., the weight loss is roughly constant at about  $7\pm 1\%$ , and from 750°–950° C. is constant at 12.8%. These weight losses, which refer to air-dry material at room temperature, will include surface adsorbed water. There is no break in the weight-loss curve at about 100° C. which would enable a distinction to be made between surface water and internal water, but if we take the weight loss at 100° C., namely 2.5%, as representing the surface water, we obtain weight losses of  $4.5\pm 1.0\%$  for the range 200°–500° C. and 10.3% for the range 750°–950° C. For a mineral with two water layers each containing 2  $H_2O$  per unit cell, a loss of 4  $H_2O$  is equivalent to a 4.6% weight loss and dehydroxylation gives a further weight loss of 6.0%, or total loss of 10.6%. These values agree well with those obtained from the weight loss measurements.

## ORGANIC COMPLEXES OF ALLEVARDITE

Caillère *et al.* (1950) showed that allevardite expands in glycerol in a manner similar to montmorillonite. In view of the precision with which the hydrated complexes could be measured, a similar study was made of complexes with dihydric alcohols. Table 6 lists results for six organic com-

TABLE 6. LATTICE SPACINGS, IN Å, OF SOME CLAY-ORGANIC COMPLEXES

1	2	3	4	5
Organic liquid	Allevardite	(2)-(4)	Montmorillonite	Stevensite
1.2 ethane diol (ethylene glycol)	26.47±0.06	9.77	16.70	17.0
1.3 propane diol	27.72±0.04	9.56	18.16	18.2
1.4 butane diol	27.19±0.07	—	—	17.3
1.5 pentane diol	27.14±0.03	9.71	17.43	18.0
1.12 polyethylene	26.73±0.10	9.62	17.11	17.3
diethylene glycol	25.42±0.04	10.07	15.35	16.7

plexes of allevardite, together with similar data for montmorillonite (a sample from Cadouin, France) and for stevensite, a montmorillonite type mineral (see Faust and Murata, 1953; Brindley, 1955). Although the number of carbon atoms in the organic molecules increases from 2 to 12, the lattice spacings remain roughly constant, in agreement with similar observations by Bradley (1945) and by MacEwan (1948). There is an obvious similarity in the general trend of the three sets of results. In every case 1.3 propane diol gives the largest expansion. MacEwan (1948, p. 359) has commented on this result and attributed it to "the extra space taken up by the central CH<sub>2</sub> group." With further increase in the number of carbon atoms, the spacing progressively diminishes.

A fourier synthesis of ethylene glycol allevardite, Fig. 4, shows the same aluminosilicate layers and bonding cations at  $z=0$  as the previous syntheses. In addition a broad peak corresponding to one layer of ethylene glycol occurs which appears to have two maxima at about 11.0 Å and 12.0 Å. The symmetry centre at  $z=c/2$  duplicates this peak, so that there are two layers of ethylene glycol separating silica layers. From the electron content of the organic peak, there are about  $1\frac{1}{2}$  molecules per layer per unit cell, which agrees with values previously given by MacEwan (1948, p. 359) and by Mackenzie (1948). The double peak in the electron distribution suggests that the (OH) groups lie at two levels. If we picture a zig-zag molecule with the plane of the zig-zag at right angles to the basal plane (see inset to Fig. 4), the vertical displacement

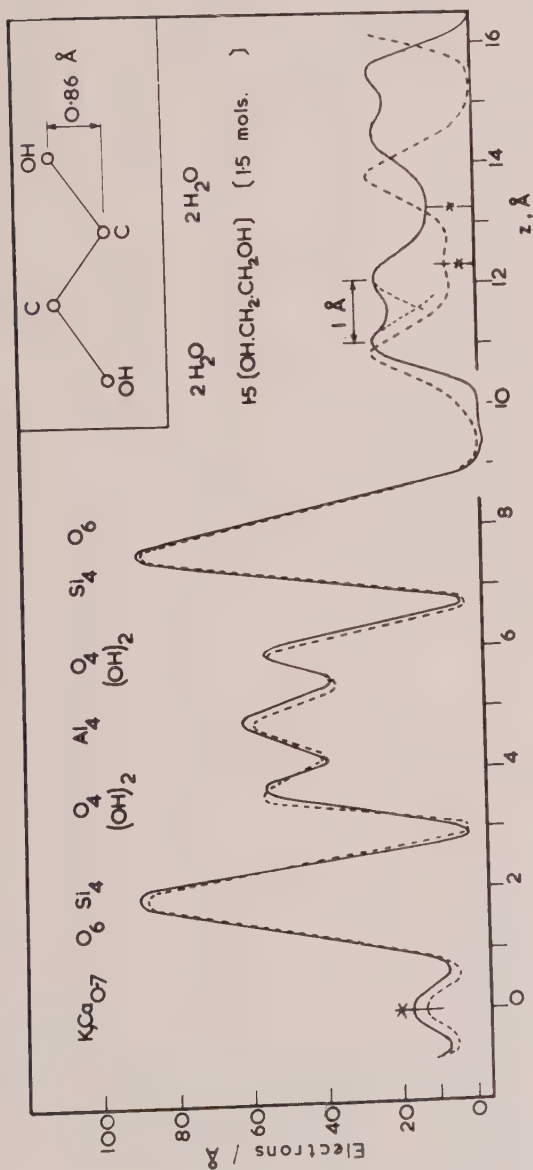


Fig. 4. Electron density distributions of ethylene glycol allevardite (full line) compared with allevardite with two water layers (dashed line). Inset shows zig-zag form of the ethylene glycol molecule. The electron distributions are continued beyond the symmetry centers, \*, to show the two layers of water and of ethylene glycol.

TABLE 7. X-RAY DATA FOR ETHYLENE GLYCOL ALLEVDARITE

$$\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$$

<i>l</i>	<i>d</i> (00 <i>l</i> ) Å	<i>d</i> (001) Å	<i>F</i>   <sub>obs</sub>	<i>F</i> <sub>calc</sub>
1	25.6	25.6*	49.0	47.5
2	13.0	26.0*	35.2	-35.2
3	8.76	26.28	20.8	-16.0
4	6.63	26.52	17.9	9.8
5	5.29	26.45	31.1	-23.5
6	4.42	26.52	20.8	-19.0
7	3.777	26.44	15.3	12.6
8	3.314	26.51	65.0	-58.9
9	2.945	26.50	39.7	-37.8
10	2.652	26.52	14.7	9.4
11	—	—	—	5.7
12	2.206	26.47	11.1	-15.1
13	2.040	26.52	30.5	23.7
14	1.895	26.53	39.7	46.6
15	1.768	26.52	9.3	15.3
16	—	—	—	-7.0
17	1.558	26.48	16.9	13.1
18	—	—	—	2.1
19	1.395	26.50	16.2	-16.4
20	1.325	26.50	15.7	-18.4
21	—	—	—	0.8
22	1.2055	26.52	14.4	27.1

Mean  $26.51 \pm 0.02$

Other values:  $26.48 \pm 0.02$

$26.37 \pm 0.08$

\* Values not incorporated in the mean value.

*F* values correspond to one-quarter of unit cell content.

of the (OH) groups is about 0.85 Å, and a slight tilt of the molecule would increase this separation to about 1 Å.

The evidence is fairly strong that the plane of the zig-zag of the glycol molecules does not lie parallel to (001) for if the molecules were so arranged, then the electron density peaks would be sharper than those observed. Table 7 compares the observed and calculated structure factors. The best agreement is obtained by dispersing the scattering matter of the organic molecules through a range of *z*-values ranging from about 11.0 to 12.0 Å. The parameters used in calculating the structure factors for this organic complex are listed in Table 5, where it is seen that  $1\frac{1}{2}$  molecules of  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  are split equally between two levels at about 11.0 and 12.0 Å.



Figure 4 compares the electron distribution in normal allevardite with two water layers (dashed line) and ethylene glycol allevardite with two organic layers (full line). It is evident that the water layers are much more sharply defined than the organic layers and that the organic peak is about twice as large as the water peak.

## ACKNOWLEDGMENTS

The writer desires to thank Mlle. Caillère for the gift of allevardite and for advance information regarding its chemical analysis.

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# OSUMILITE, A NEW SILICATE MINERAL, AND ITS CRYSTAL STRUCTURE\*

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## ABSTRACT

Osumilite (K, Na, Ca)(Mg, Fe<sup>+2</sup>)<sub>2</sub>(Al, Fe<sup>+3</sup>, Fe<sup>+2</sup>)<sub>3</sub>(Si, Al)<sub>12</sub>O<sub>30</sub>·H<sub>2</sub>O is dihexagonal-dipyramidal ( $6/m\ 2/m\ 2/m = D_{6h}$ ). Space group  $P\ 6/mcc = D_{6h}^2$ . Unit cell:  $a_0 = 10.17\ \text{\AA}$ ,  $c_0 = 14.34\ \text{\AA}$ ;  $a_0:c_0 = 1:1.410$ ; containing two molecules. The crystals are black, prismatic or tabular.  $G = 2.64$ . Uniaxial positive. Indices of refraction (for Na):  $\omega = 1.545 - 1.547$ ,  $\epsilon = 1.549 - 1.551$ ;  $\epsilon - \omega = 0.004$ . Dichroic with  $\omega =$  light blue and  $\epsilon =$  colorless.

Structurally, osumilite is composed of hexagonal double rings (Si, Al)<sub>12</sub>O<sub>30</sub>, connected by metal atoms (Al, Fe<sup>+3</sup>, Fe<sup>+2</sup>) in 4-coordination, (Mg, Fe<sup>+2</sup>) in 6-coordination, and (K, Na, Ca) in 12-coordination. It is iso-structural with milarite.

Osumilite was found in a volcanic rock at Sakkabira, Kyusyu, Japan, and is named after the province Ōsumi. Probably osumilite is a relatively common mineral, but always has been mistaken for cordierite. It appears to occur characteristically in volcanic rocks and inclusions in them.

## INTRODUCTION

Many mineralogists have tried unsuccessfully to correlate the optical properties of cordierites with their chemical compositions. The writer thought that the difficulty in correlation might be due, at least partly, to the existence of polymorphism in cordierite. This thought prompted him to begin a study of cordierite. It was soon found that there is a close relationship between the modes of occurrence and the optical properties of the mineral. Of particular interest is the fact that nearly or completely uniaxial positive cordierite is reported to occur characteristically in volcanic rocks. The writer considered that such material might represent a high-temperature form of cordierite. Then, he examined a uniaxial positive "cordierite" from a volcanic rock in Sakkabira, Hayasaki, Tarumizumati, Kimotuki-gun, Kagosima Prefecture, Kyusyu (Kyushu), Japan, and found that it is not cordierite, but actually is a new *hexagonal* mineral, here named *osumilite* after Ōsumi, the name of an old province in Sakkabira.

The locality is near the southeastern foot of the famous volcano Sakurazima (Sakurajima). Morimoto (1948) and Morimoto and Minato (1949) described the mode of occurrence, physical properties, and chemical composition of the mineral in detail, though they considered it to be cordierite. The writer owes very much to their descriptions.

\* Contribution from the Department of Mineralogy and Petrography, Harvard University, number 357.

## MODE OF OCCURRENCE

According to Morimoto and Minato (1949), the osumilite occurs in biotite-bearing hypersthene plagioliparite (rhyodacite) which contains andesine, quartz, hypersthene, biotite, and magnetite as phenocrysts scattered in the groundmass. Yamaguchi (1938) gives three chemical analyses of the rock in this neighborhood, the ranges of each component being given in Table 1.

Osumilite is present in the brittle porous part of the plagioliparite

TABLE 1. COMPOSITION RANGE OF BIOTITE-BEARING HYPERSTHENE  
PLAGIOLIPARITE NEAR SAKKABIRA, KYUSYU

SiO <sub>2</sub>	72.75-74.65
Al <sub>2</sub> O <sub>3</sub>	13.67-14.54
Fe <sub>2</sub> O <sub>3</sub>	0.40- 0.64
FeO	1.43- 1.92
MgO	0.61- 0.67
MnO	0.04
CaO	2.66- 2.77
Na <sub>2</sub> O	3.05- 4.23
K <sub>2</sub> O	2.16- 2.50
TiO <sub>2</sub>	0.13- 0.17
P <sub>2</sub> O <sub>5</sub>	0.07- 0.26
H <sub>2</sub> O+	0.24- 0.47
H <sub>2</sub> O-	0.02- 0.39

and not in the hard compact portion. Euhedral crystals occur in association with tridymite and quartz in drusy cavities in the brittle porous part, whereas anhedral crystals occur in the groundmass. The groundmass is comparatively highly crystalline, and is composed mainly of tridymite, oligoclase and alkali feldspar, with small quantities of glass ( $n=1.487-1.492$ ), quartz, fayalite ( $\alpha=1.800$ ,  $2V(-)=56^\circ$ ), hypersthene ( $\gamma=1.720$ ), biotite ( $\gamma=1.608$ ), osumilite, and iron oxide dust.

Osumilite crystallized from the plagioliparite magma at the final stage of consolidation.

## PHYSICAL PROPERTIES

Osumilite occurs in crystals, a few millimeters or less in size, black to the unaided eye, and prismatic or tabular in habit. Neither cleavage nor twinning was observed. The specific gravity is 2.64 as determined by suspending the mineral in a mixture of bromoform and acetone.

Under the microscope, osumilite is nearly or completely uniaxial positive. The refractive indices are (for Na):

$$\omega=1.545-1.547$$

$$\epsilon=1.549-1.551$$

$$\epsilon-\omega=0.004$$

It shows remarkable dichroism as follows:

$$\epsilon(\parallel c) = \text{colorless}$$

$$\omega(\perp c) = \text{light blue}$$

### UNIT CELL AND SPACE GROUP

Laue, rotation, Weissenberg and powder photographs of osumilite were taken, using  $\text{CuK}\alpha$  radiation throughout the experiments. The powder data are shown in Table 2.

TABLE 2. X-RAY POWDER DATA OF OSUMILITE

Intensities	$d(\text{\AA})$	Indices
VW	8.8	1010
S	7.17	0002
W	5.55	10\bar{1}2
S	5.08	1120
M	4.41	2020
S	4.15	11\bar{2}2
M	3.74	2022
W	3.58	0004
W	3.34	12\bar{3}0, 10\bar{1}4
VS	3.24	12\bar{3}1
W	3.02	1232
S	2.930	11\bar{2}4, 30\bar{3}0
M	2.776	2024
W	2.543	4220
W	2.390	0006
W	2.170	
W	2.016	
M	1.855	
W	1.737	
VW	1.462	
W	1.437	
W	1.406	

Laue and Weissenberg photographs show that it is hexagonal in symmetry. The unit cell has the dimensions:

$$a_0 = 10.17 \text{ \AA}$$

$$c_0 = 14.34 \text{ \AA}$$

$$a_0:c_0 = 1:1.410$$

The reflections  $(hh2hl)$  and  $(h0\bar{h}l)$  were observed only when  $l = \text{even}$ . Thus, the space group is  $P 6_1/mcc = D_{6h}^2$  or  $P 6cc = C_{6i}^2$ . As will be shown in the next section, the writer succeeded in determining the crystal structure of osumilite by assuming the existence of a center of symmetry. We may then consider that the space group is probably  $P 6/mcc$ .



## CHEMICAL FORMULA AND CRYSTAL STRUCTURE

A chemical analysis of prismatic crystals of osumilite by Minato is given in Table 3. A simple calculation from the analysis, unit cell dimensions, and specific gravity reveals that the unit cell contains 60 oxygen atoms (except those constituting H<sub>2</sub>O molecules). Then, in the third

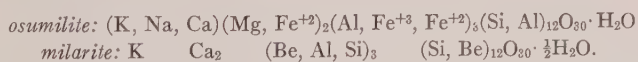
TABLE 3. CHEMICAL ANALYSIS OF OSUMILITE

	Wt. %	Mol. prop.	Atomic ratios (O=30)	
SiO <sub>2</sub>	50.78	8455	9.01	12.00
Al <sub>2</sub> O <sub>3</sub>	24.85	2438	5.20	
TiO <sub>2</sub>	0.01	1	0.00	3.39
Fe <sub>2</sub> O <sub>3</sub>	1.95	122	0.26	
FeO	9.97	1388	1.48	17.78
			0.56	
MgO	6.68	1657	1.77	2.39
MnO	0.40	56	0.06	
CaO	0.61	109	0.12	0.79
Na <sub>2</sub> O	1.00	161	0.35	
K <sub>2</sub> O	1.42	151	0.32	H <sub>2</sub> O 1.03
H <sub>2</sub> O+	1.73	962		
H <sub>2</sub> O-	0.27			
	99.67			

Note. BeO is absent according to a spectrographic analysis by H. C. Harrison.

column of the Table, the content of atoms in half a unit cell is shown on the basis of 30 oxygen atoms.

Osumilite has unit cell dimensions similar to milarite in which  $a_0 = 10.5 \text{ \AA}$  and  $c_0 = 13.9 \text{ \AA}$  (Belov and Tarkhova, 1949; Ito, Morimoto and Sadanaga, 1952). Osumilite has the same space group and the same number of oxygen atoms in the unit cell as milarite. The chemical formula of osumilite can be written in the form corresponding to that of milarite as follows:



Moreover, the rotation and Weissenberg photographs of the two minerals show remarkable similarity, especially in reflections at smaller angles. Therefore, it is considered that osumilite is iso-structural with milarite.

The parameters of atoms in osumilite were determined by the method of trial and error. Intensities of reflections were estimated visually, and converted into numerical values on an arbitrary scale. They are cor-

TABLE 4. COORDINATES OF ATOMS IN OSUMILITE

No. of the equivalent atoms of the unit cell	Atoms	<i>x</i>	<i>y</i>	<i>z</i>
2	K, Na, Ca	0	0	$\frac{1}{4}$
2	H <sub>2</sub> O	0	0	0
4	Mg, Fe	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
6	Al, Fe	$\frac{1}{2}$	0	$\frac{1}{4}$
24	Si, Al	0.10	0.35	0.11
12	O <sub>I</sub>	0.13	0.42	0
24	O <sub>II</sub>	0.21	0.29	0.12
24	O <sub>III</sub>	0.13	0.47	0.17

rected for the Lorentz and polarization factors, but not for extinction nor absorption. At the final stage of structure analysis, these values were rendered comparable with corresponding calculated values by multiplying by an appropriate number which minimizes the differences between observed and calculated values.

The agreement between observed and calculated structure amplitudes is good with the parameter values shown in Table 4. The atomic scattering factors used are shown in Table 5, and observed and calculated structure amplitudes are shown in Table 6.

The structure of osumilite is based on hexagonal double rings (Si, Al)<sub>12</sub>O<sub>30</sub>, each of which is composed of 12 (Si,Al)—O tetrahedra, as shown in Fig. 1. The two horizontal reflection planes of the unit cell (0.00 and 0.50 high) pass the central position of each double ring. The plan of the lowest quarter of the unit cell is shown in Fig. 2, which reveals how those double rings are linked by (Al,Fe<sup>+3</sup>,Fe<sup>+2</sup>) atoms in 4-coordination, by (Mg,Fe<sup>+2</sup>) atoms in 6-coordination and (K,Na,Ca) atoms in 12-coordination. H<sub>2</sub>O molecules are inside the double rings. Probably the water content is not essential to this mineral, and the quantity of (K,Na,Ca) is variable to some extent.

TABLE 5. ATOMIC SCATTERING FACTORS

$\frac{\sin \theta}{\lambda} \times 10^{-3}$	0	0.2	0.4	0.6	0.8	1.0
K, Na, Ca	14.0	11.0	7.1	5.1	4.1	3.3
Mg, Fe	13.5	11.2	7.8	5.4	3.9	3.1
Al, Fe	14.6	12.2	8.9	6.4	4.7	3.6
Si, Al	10.0	9.1	7.0	4.9	3.3	2.5
O and H <sub>2</sub> O	10.0	5.5	2.7	1.8	1.5	1.3

TABLE 6. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

$hk \cdot l$	$F_0$	$ F_c $	$hk \cdot l$	$F_0$	$ F_c $
00.2	112	98	22.0	153	185
00.4	195	204	32.0	68	49
00.6	39	78	42.0	96	127
00.8	340	358	52.0	201	164
00.10	80	82	33.0	123	120
00.12	45	67	43.0	41	27
00.14	317	248	53.0	14	5
00.16	169	142			
			10.2	38	64
10.0	9	4	10.4	72	68
20.0	43	40	10.6	9	26
30.0	55	75	10.8	25	35
40.0	9	21	10.10	13	22
50.0	168	168	10.12	32	56
60.0	50	56	20.2	66	112
70.0	129	78	20.4	176	197
80.0	164	124	20.6	0	4
90.0	76	122	20.8	36	29
10,0.0	12	15	20.10	60	116
			30.2	8	11
11.0	64	124	30.4	9	13
21.0	15	58	30.6	67	76
31.0	43	70	30.8	76	79

As is shown in Table 3, the total number of metal atoms, Si, Al, Fe, Mg, and Mn, calculated from the actual analysis on the basis of O=30, is 17.78. It is a little larger than that expected from the theoretical formula (17.00). This may be due to the following reasons:

(1) The sample for chemical analysis was not pure, or the analysis was not sufficiently accurate.

(2) Some of the above mentioned metal atoms may occupy some other positions.

(3) Some of the hydrogen atoms which are so far provisionally calculated as forming H<sub>2</sub>O molecules, may actually be present as (OH) ions connected with Si atoms. (In milarite only one half of the total available space for water molecules is statistically filled.)

#### MORPHOLOGY

The crystallographic axes  $a_1$  and  $a_2$  are determined so as to be parallel to horizontal edges of the unit cell. Goniometric data are given in Table 7. Crystals of osumilite are generally a few millimeters or less in size, but rarely reach 5 millimeters in longest dimension. Commonly they are short

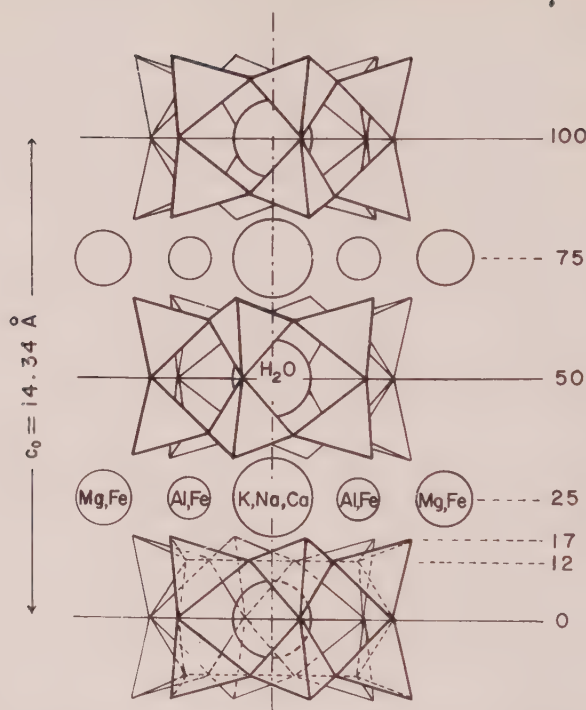


FIG. 1. Hexagonal double rings, projected on (0110). Figures give heights by a percentage of the  $c$ -translation.

prismatic, being elongated parallel to the  $c$ -axis, or tabular on  $\{0001\}$ . Usually they have well-developed faces of forms:  $c\{0001\}$ ,  $m\{10\bar{1}0\}$ , and  $a\{11\bar{2}0\}$ . Generally the faces of  $a\{11\bar{2}0\}$  are much larger than those of  $m\{10\bar{1}0\}$ . The faces of  $j\{21\bar{3}0\}$  are common, though they are usually very small.

TABLE 7. TWO CIRCLE GONIOMETRIC MEASUREMENTS OF OSUMILITE

Form	Measured		Calculated ( $p_0 = 1.634$ )		No. of faces	No. of crystals	Size	Quality
	$\phi$	$\rho$	$\phi$	$\rho$				
$c$ 0001		0° 00'		0° 00'	2	2	large	good
$m$ 10 $\bar{1}0$	29° 45' -30° 00'	89° 52' -90° 08'	30° 00'	90° 00'	12	2	medium	good
$a$ 11 $\bar{2}0$	0° 00'	89° 35' -90° 16'	0° 00'	90° 00'	12	2	large	good
$j$ 21 $\bar{3}0$	10° 49' -11° 01'	89° 40' -90° 03'	10° 54'	90° 00'	16	2	very small	fair
$p$ 10 $\bar{1}1$	29° 52' -29° 55'	57° -60°	30° 00'	58° 32'	4	1	very small	bad
$q$ 10 $\bar{1}2$	29° 52' -30° 00'	38° -39° 15'	30° 00'	39° 15'	7	2	small	poor
$e$ 11 $\bar{2}2$	0° 00'	54°	0° 00'	54° 45'	2	1	very small	bad



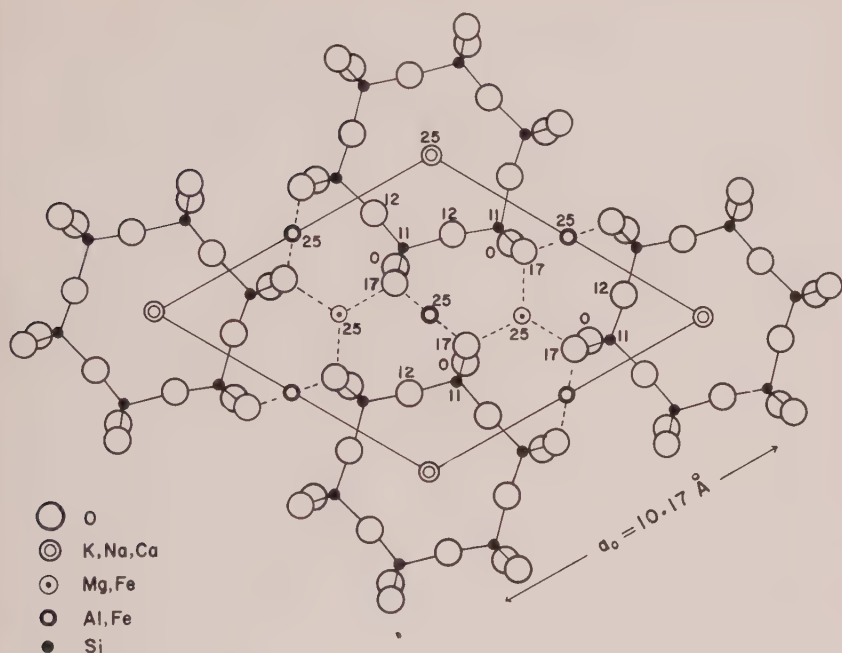


FIG. 2. The lowest quarter of a unit cell of osumilite, projected on (0001). The height of each atom is given by a percentage of the  $c$ -translation. (Si, Al) bonds to oxygen are shown as solid lines, and other bonds are shown as broken lines.

Dipyramidal faces  $p\{10\bar{1}1\}$  and  $e\{11\bar{2}2\}$  are not rare, but frequently very small in size and bad in quality of reflection. Dipyramidal faces  $q\{10\bar{1}2\}$  are rare in prismatic crystals but not rare in tabular ones, in which sometimes they are medium in size, but their quality of reflection is not good. Certain faces are frequently composed of a few to many vicinal faces.

As the quality of reflection of the dipyramidal faces is not good, a precise determination of the axial ratio from the goniometric data is difficult. Fortunately a dipyramidal face  $(10\bar{1}2)$  showing relatively good reflection was found, and gives the values:

$$\phi = 30^\circ 00', \rho = 39^\circ 15'; \text{ and then } a:c = 1:1.415.$$

This is in good agreement with the ratio  $a_0:c_0 = 1:1.410$  as determined by an  $x$ -ray method.

#### COMPARISON WITH CORDIERITE

Osumilite is composed of hexagonal double rings  $(\text{Si,Al})_{12}\text{O}_{30}$ , while cordierite is composed of pseudo-hexagonal single rings  $(\text{Si,Al})_6\text{O}_{18}$ . There-

fore,  $a_0$  of osumilite is similar to  $b_0$  of cordierite, while  $c_0$  of osumilite is much longer than that of cordierite (Table 8). Thus, the most reliable method of distinction between osumilite and cordierite is in the measurement of unit cell dimensions. Their x-ray powder patterns are also entirely different.

Osumilite and cordierite have similar refractive indices, but the birefringence of osumilite is lower. Osumilite is nearly or completely uni-

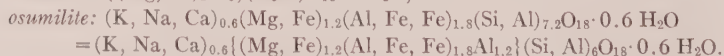
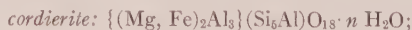
TABLE 8. COMPARISON OF CORDIERITE WITH OSUMILITE

	<i>Cordierite</i>	<i>Osumilite</i>
$a_0$	17.1 Å	10.17 Å
$b_0$	9.7 Å	—
$c_0$	9.3 Å	14.34 Å
Refr. indices	$\begin{cases} \alpha = 1.52-1.56 \\ \gamma = 1.53-1.57 \end{cases}$	$\begin{cases} \omega = 1.545-1.547 \\ \epsilon = 1.549-1.551 \end{cases}$
Birefringence	0.008-0.016	0.004
2V over $\gamma$	Usually 75°-140°	Usually 0°

axial positive, while cordierite is biaxial positive or negative with a large optical angle. Thus the measurement of optical angles is an important way of differentiation.

Osumilite is more deeply colored than, at least, most cordierites. Osumilite is black to the unaided eye and light blue in ordinary thin sections. Even when cordierite is rich in iron, it is usually colorless in ordinary thin sections, as is exemplified by iron-cordierites from Sasago and Dosi (Shibata, 1936), or by artificial iron-cordierites (Richardson and Rigby, 1949; Schairer and Yagi, 1952).

Osumilite and cordierite have different chemical formulas, but when the weight percentages are compared in analytical tables, the difference is very small and might be overlooked. In Table 9 are shown analyses of osumilite and of two cordierites. If we erroneously calculate an analysis of osumilite to the formula of cordierite (that is, on the basis of 18 oxygen atoms), the following discrepancy appears:



Thus, an analysis of osumilite should give a total number of Al, Fe, Mg, and Mn atoms which do not belong to hexagonal rings, equal to 4.2, that is smaller than 5 in true cordierite. The writer calculated this value from many available actual analyses of cordierites and found it to range from 4.87 to 5.11, while the value from the actual analysis of

TABLE 9. CHEMICAL ANALYSES OF CORDIERITE AND OSUMILITE

	I	II	III	IV	V
SiO <sub>2</sub>	49.50	48.19	50.78	48.32	49.15
Al <sub>2</sub> O <sub>3</sub>	32.45	33.45	24.85	22.13	31.84
TiO <sub>2</sub>	0.06	0.01	0.01	n.d.	n.d.
Fe <sub>2</sub> O <sub>3</sub>	0.40	0.55	1.95	3.88	2.88
FeO	8.90	8.40	9.97	9.58	11.49
MgO	6.73	7.95	6.68	9.10	0.55
MnO	0.11	0.18	0.40	0.68	n.d.
CaO	0.57	0.17	0.61	4.95	4.30
Na <sub>2</sub> O	0.46	0.22	1.00	n.d.	n.d.
K <sub>2</sub> O	0.39	0.02	1.42	n.d.	n.d.
H <sub>2</sub> O+	0.62	0.67	1.73	} 1.54	} 0.06
H <sub>2</sub> O—	—	0.01	0.27		
	100.19	99.82	99.67	100.18	100.27

I. Cordierite from Laramie Range, Albany County, Wyoming (Newhouse and Hagner, 1949).

II. Cordierite from Great Slave Lake, Canada (Folinsbee, 1941).

III. Osumilite from Sakkabira, Japan.

IV. Ca-rich "cordierite" (or Ca-rich osumilite) from Laacher See, Germany (Gossner and Reindl, 1932).

V. Ca-rich "cordierite" (or Ca-rich osumilite) from Celebes (Bücking, 1900).

osumilite is 4.68. The discrepancy between the theoretical value 4.2 and the actual value 4.68, is due to a slightly too large total number of metal atoms Si, Al, Fe, Mg, and Mn, as stated and discussed previously. Cordierite is variable in alkali and H<sub>2</sub>O contents, and that may also be true of osumilite.

#### OCCURRENCE OF OSUMILITE IN GENERAL

Probably osumilite is a relatively common mineral, but has always been mistaken for cordierite. So far as the writer is aware, osumilite occurs characteristically in volcanic rocks and inclusions in them.

For example, Taneda (1950) described a "cordierite" with small positive optical angles in the groundmass of a hypersthene-rhyodacite from Hamanoiti, Kagosima Prefecture, Kyusyu. It is in anhedral crystals, less than 0.5 millimeter in diameter, pleochroic from light blue to colorless. This is probably osumilite, showing anomalous biaxial character, if the description is accurate. Recently M. Yamasaki and the writer found a uniaxial positive mineral which is probably osumilite from a volcanic rock in Isigami-yama, Kumamoto Prefecture, Kyusyu.

In the literature the writer found two analyses of "cordierites"

which may actually represent osumilite. They are "cordierite" from the Laacher See district described by Brauns (1911) and later analyzed by Gossner and Reindl (1932), and "cordierite" from Celebes described by Bücking (1900). They both occur in ejecta from volcanoes.

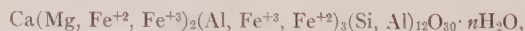
Brauns described the former as being newly formed in an ejecta, and being nearly uniaxial positive. Bücking described the latter as occurring in six-sided prismatic crystals, pleochroic from colorless ( $\parallel c$ ) to light bluish purple ( $\perp c$ ). Their compositions, which are shown in Table 9, are abnormal for cordierite as indicated by the describers themselves. They both contain a very large amount of CaO. No other cordierites in the literature show such a large content of CaO. When we calculate the compositions to the formula of cordierite, the total numbers of Al, Fe, Mg, and Mn atoms which do not belong to hexagonal rings, are too small (4.67 and 4.35 respectively) when compared with that for cordierite

TABLE 10. COMPOSITIONS OF CA-RICH OSUMILITES

Locality	I		II	
	Laacher See		Celebes	
O	30.00		30.00	
Si	8.65	3.35	8.55	3.45
Al	4.67		6.51	
Fe <sup>+3</sup>	0.52	1.32	0.38	3.06
Fe <sup>+2</sup>	1.43		1.67	
Mg	2.42	2.52	0.15	2.20
Mn	0.10			
Ca	0.95	0.95	0.80	0.80
H <sub>2</sub> O	0.92	0.92	0.03	0.03

(4.87-5.11). If we calculate them to the formula of osumilite, however, the Laacher See "cordierite" shows fairly good agreement with the formula, and the Celebes "cordierite" is very close, as shown in Table 10.

These comparisons suggest that actually they may represent Ca-rich osumilites, which have the formula:



where  $n=0-1$ . Bücking observed a twin-like structure in the Celebes mineral under the microscope. But it may be only apparent, like the similar structure in milarite (Ito, Morimoto, and Sadanaga, 1952).

#### ACKNOWLEDGMENTS

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#### POSTSCRIPT

This paper was written in the spring of 1953, when the writer was temporarily at Harvard University. Owing to the loss of the manuscript in transit, its publication has been delayed. (The drawings of osumilite crystals were lost as a result of the accident.) In 1954, the writer and his coworkers in Tokyo University found that so-called "artificial cordierite" formed in synthetic experiments and industrial processes is not true cordierite, but actually a hexagonal polymorph of cordierite composition. As they found this polymorph to occur in a rock in India, they gave it the name "indialite." The "artificial iron-cordierite" synthesized by Schairer and Yagi (1952), which is referred to in this paper, is actually iron-indialite. Refer to "A preliminary note on a new mineral, indialite, polymorphic with cordierite" by A. Miyashiro and T. Iiyama (*Proc. Japan Acad.*, **30**, 746-751, 1954), and also to "The polymorphism of cordierite and indialite" by A. Miyashiro, T. Iiyama, M. Yamasaki, and T. Miyashiro (*Am. Jour. Sci.*, **253**, 185-208, 1955).

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# OSCILLATING-HEATING X-RAY DIFFRACTOMETER STUDIES OF CLAY MINERAL DEHYDROXYLATION<sup>1</sup>

E. J. WEISS<sup>2</sup> AND RICHARDS A. ROWLAND<sup>3</sup>

## ABSTRACT

With an oscillating-heating *x*-ray-diffraction technique the position and intensity of an *x*-ray diffraction maximum may be followed continuously while a powdered sample is heated at a regular rate of temperature rise (5° C. per minute). The sample is sedimented on a platinum slide mounted in a furnace designed to fit the horizontal shaft of the North American Philips *X*-ray Diffractometer. The diffractometer is set with the maximum to be followed at the center of one-half degree  $2\theta$  oscillation. After heating and oscillating the tops of the recorded series of peaks indicate position and intensity. The bottoms represent the background which is very sensitive to position changes.

Typical oscillation-heating patterns of basal spacing maxima for Georgia kaolinite, a Vermont chlorite, a clinochlore, and sheridanite are presented. The kaolinite (001) remains constant at 12.32  $2\theta$  until it collapses at 525° C. The chlorites (002) shift from 12.55°  $2\theta$  to 12.42°  $2\theta$  and begin to collapse simultaneously with the intensity increase of the (001).

Sheridanite (001) increases abruptly at 575° C. and collapses at 850° C. after shifting from 6.28° to 6.49°  $2\theta$ . Clinochlore follows a similar pattern. The (002) collapses abruptly at 575° C. Vermont chlorite (001) begins the intensity increase at 600° C., is greatest at 780° C., begins to collapse at 840° C., and is collapsed at 910° C. after shifting from 6.28°  $2\theta$  to 6.52°  $2\theta$ . The (002) collapse begins at 600° C. and is complete at 910° C. These differences may be related to the iron content of the brucite layer.

## INTRODUCTION

The *x*-ray diffraction technique described in this paper fills a gap in the available methods for distinguishing by *x*-ray diffraction between two similar but slightly different materials. It has long been the practice among investigators to apply the principle, "if it is solid, heat it, and if it is liquid, freeze it," to difficult diffraction problems. Stepwise heating often loses the beginning of phase changes, the fine detail of which is important to the final analysis. Actually, the real need is a method for obtaining a complete diffraction pattern instantaneously at any temperature; but for reasons of geometry and sensitivity of the registering devices for the scattered *x*-rays, such a method is not feasible presently. However, by oscillating the diffractometer over a sufficient number of diffraction maxima while the temperature is increased at a regular rate, a series of diagrams may be obtained which represent the diffraction pattern at any temperature within the range. This technique can be extremely useful with many materials. Here it has been applied to three

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chlorites and a kaolinite because of their importance in fine grained sediments. The chlorites, with the great intensity increase of the (001) maximum, make a most spectacular demonstration of the ability of the heating-oscillation technique to furnish a continuous record of changes in the diffraction pattern at every temperature within the range.

#### DESCRIPTION OF APPARATUS

The diffractometer furnace and the oscillation technique were developed at the Shell Development Research Laboratory. Many of the details were adapted from a furnace built by Birks and Friedman (1947)

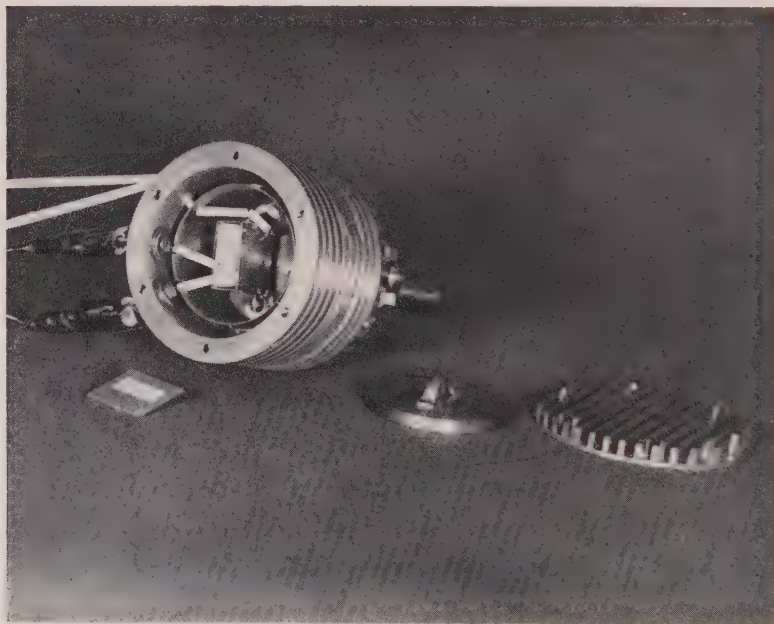


FIG. 1. Assembled view of heating-oscillating furnace.

at the U. S. Naval Research Laboratory.<sup>4</sup> The furnace, shown ready for mounting in Fig. 1, consists of a brass cassette enclosing a cylindrical nickel shield. Openings in the cassette and the shield are aligned for the passage of the x-ray beam. A platinum case fastened inside the nickel shield holds the furnace and the sample.

The heating element consists of No. 30 *B* and *S* gauge 87 per cent platinum, 13 per cent rhodium wire which is wound on two-hole, one-

<sup>4</sup> Birks, L. S., and Friedman, H., A high temperature x-ray diffraction apparatus: *Rev. of Sci. Instruments*, **18**, 578-580 (1947).

inch long alundum thermocouple tubes ( $OD \frac{3}{8}$  inch). The coils are welded together in series and are mounted in alundum cement. The entire coil assembly, 1 inch by 1 inch by  $\frac{1}{2}$  inch, is attached to the spindle of the diffractometer head by means of an insulating block. A parallel motion adjustment screw incorporated in the assembly allows alignment of the specimen.

#### EXPERIMENTAL PROCEDURE AND RESULTS

The sample is sedimented or smeared on a platinum plate on which a platinum 10 per cent rhodium thermocouple is welded. The mounted sample is placed in the holder over the furnace and a preliminary run is made at room temperature to locate the position of the diffraction maxima. The goniometer is then set to oscillate over the maximum to be scanned. The range of the oscillation is set to cover any possible shift in the position of the diffraction maximum and still be as short as possible. The oscillation limits are adjusted so that the backgrounds of the maximum through the upscale and downscale oscillations are at the same level on the chart. The temperature of the furnace is raised at a regular rate, while a record is made of changes in the height and position of the diffraction maximum.

This oscillation and heating technique permits the detection of slight changes in  $2\theta$ , because a small change in the position of the diffraction maximum is exaggerated on the tracing. When the maximum is at the midpoint of the upscale or downscale oscillation, there is a definite background height for this maximum; and since the oscillation is set over the upper portion of the maximum, a shift in  $2\theta$  changes the height of the background. The background height is increased in one direction of oscillation and decreased in the other. These combined displacements of the upscale and downscale maxima emphasize any slight shift in position.

*Kaolinite, Bath, South Carolina.* The oscillation tracings of the first and second order basal diffraction maxima of a South Carolina kaolinite are shown in Fig. 2. The breakdown of the two maxima is abrupt at  $525^\circ \text{C}$ . There is only barely perceptible shift in the position of the  $7 \text{ \AA}$  maximum toward larger spacing, but the effect is clearly apparent in the second order. Only trivial expansion and abrupt simultaneous disappearance are indicated. The abrupt breakdown of the basal diffraction maxima and the essentially steady position of the  $7 \text{ \AA}$  spacing throughout the temperature range of its stability appear to be typical of kaolinite.

*Sheridanite, Sheridan County, Wyoming.* The oscillation tracings of sheridanite are shown in Fig. 3. The first-order basal diffraction max-



## KAOLINITE

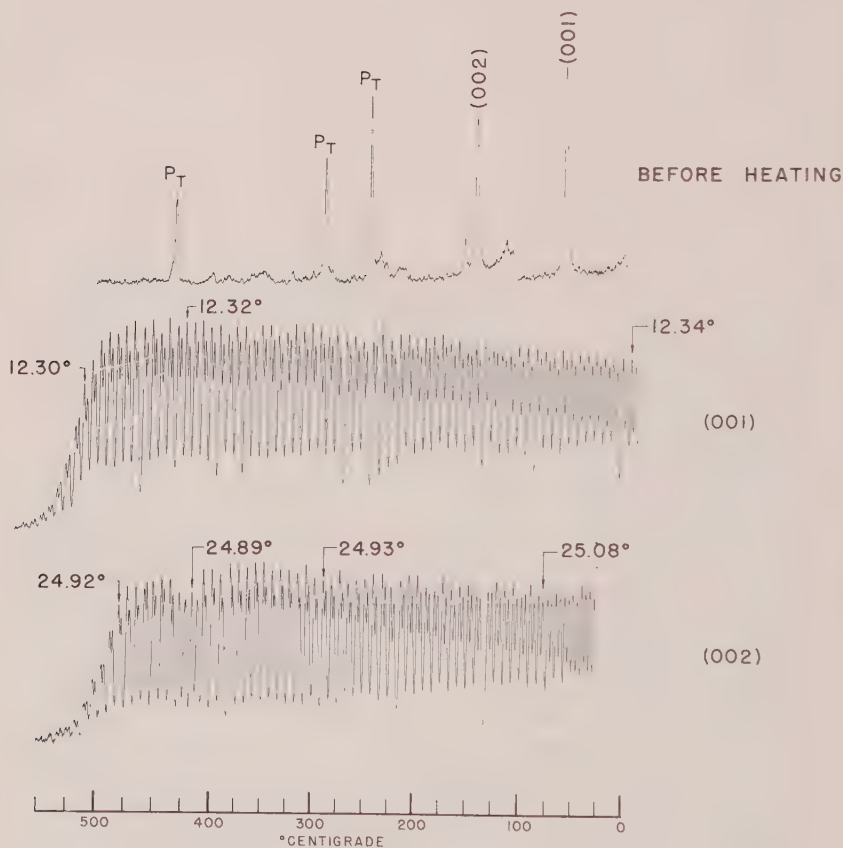


FIG. 2. Heating-oscillating patterns of the first and second order of the basal spacing of kaolinite.

imum ( $14 \text{ \AA}$ ) increases in intensity abruptly near  $575^\circ \text{ C.}$ , the temperature at which there is the greatest decrease in the intensity of the  $7 \text{ \AA}$  maximum. The position of the (001) diffraction maximum changes from  $6.28^\circ 2\theta$  to  $6.49^\circ 2\theta$  with the greatest shift between  $600^\circ \text{ C.}$  to  $850^\circ \text{ C.}$  On the (001) tracing of sheridanite, the background of the upscale maximum is lower than that for the downscale (the  $2\theta$ -angles are marked for the maximum on the travel of the geiger tube toward a higher angle) because the goniometer was set so that the position of the upscale maximum was nearer the low-angle limit of the oscillation. This setting compensated for the normal shift of the  $14 \text{ \AA}$  maximum toward a larger

angle and kept both the upscale and downscale maxima within the oscillation range. The divergence of the backgrounds is constant up to 600° C. Over a short temperature range, slightly above 600° C. to 620° C., the upscale and downscale backgrounds are at the same level, indicating that the maximum is at the center of the oscillation range. At 625° C. the backgrounds begin to diverge. This shift in the position of the maximum is greatest at the temperature of its decrease in intensity. At 850° C. the upscale position is only slightly below the upper limit of the goniometer oscillation. At higher temperatures this maximum disappears.

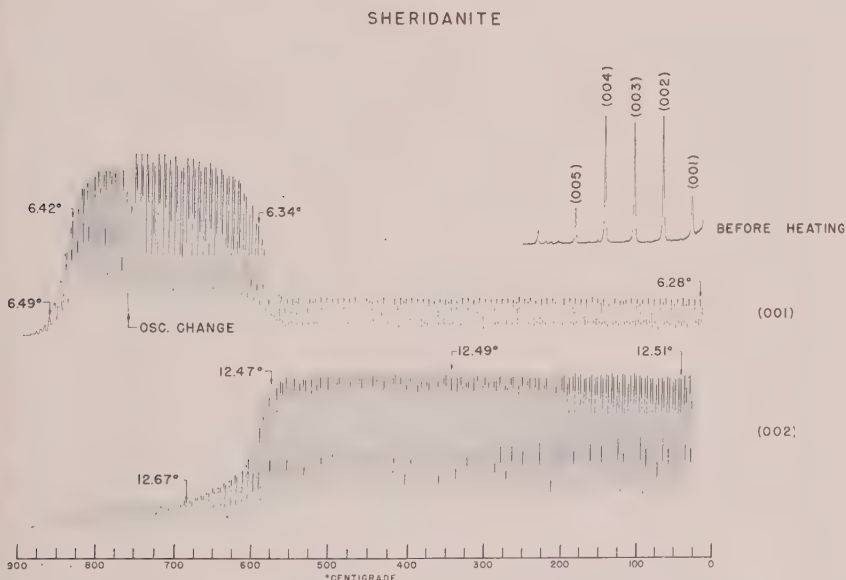


FIG. 3. Heating-oscillating patterns of two orders of the basal spacing of sheridanite.

During the oscillation over the (002) basal maximum of sheridanite, Fig. 3, the limits of the geiger tube travel were set so that the 7 Å maximum was close to the upper limit of the oscillation. This compensates for the migration of the maximum to smaller  $2\theta$ . The shift is from 12.51°  $2\theta$  at room temperature to 12.47°  $2\theta$  at approximately 580° C. and is greatest in the temperature range of the abrupt decrease in intensity of the maximum. The two backgrounds are at nearly the same level from 580° C. to the temperature at which the maximum collapses, indicating that the position of the maximum is nearly constant between 580° C. and 875° C. Characteristics of oscillation tracings of sheridanite are: the 7 Å and 14 Å maxima each finally collapse at the same temperature,

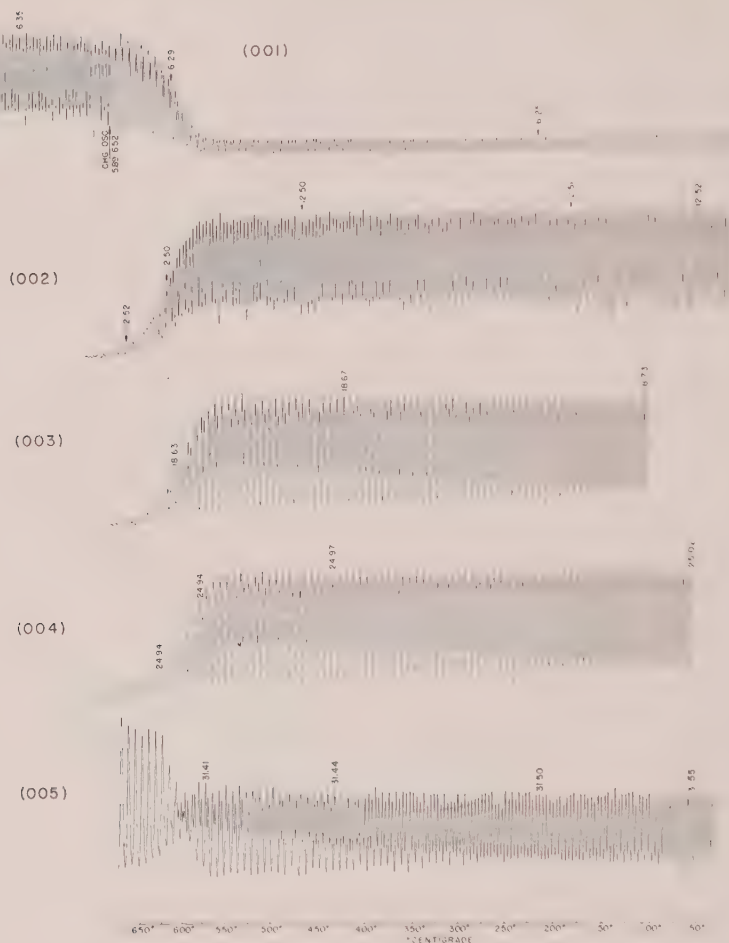


FIG. 4. Heating-oscillation patterns of five orders of the basal spacing of clinocllore.

the rise and fall in intensity of the  $14 \text{ \AA}$  maximum is abrupt, and the  $7 \text{ \AA}$  maximum after an initial abrupt collapse gradually declines until the final disappearance about  $875^\circ \text{ C}$ .

*Clinocllore.* The oscillation tracings of the first, second, third, fourth and fifth orders (00 $l$ ) basal diffraction maxima are shown in Fig. 4. The (001) maximum increases in intensity at  $575^\circ \text{ C}$ ., collapses at  $850^\circ \text{ C}$ ., and shifts toward a smaller spacing. The (002) and (003) maxima also shift, the (002) migrating toward a larger spacing, and the (003) shifting slightly toward a smaller spacing. The (002) and (003) collapse at  $640^\circ \text{ C}$ ., a temperature  $210^\circ \text{ C}$ . below the collapse of the  $14 \text{ \AA}$  max-

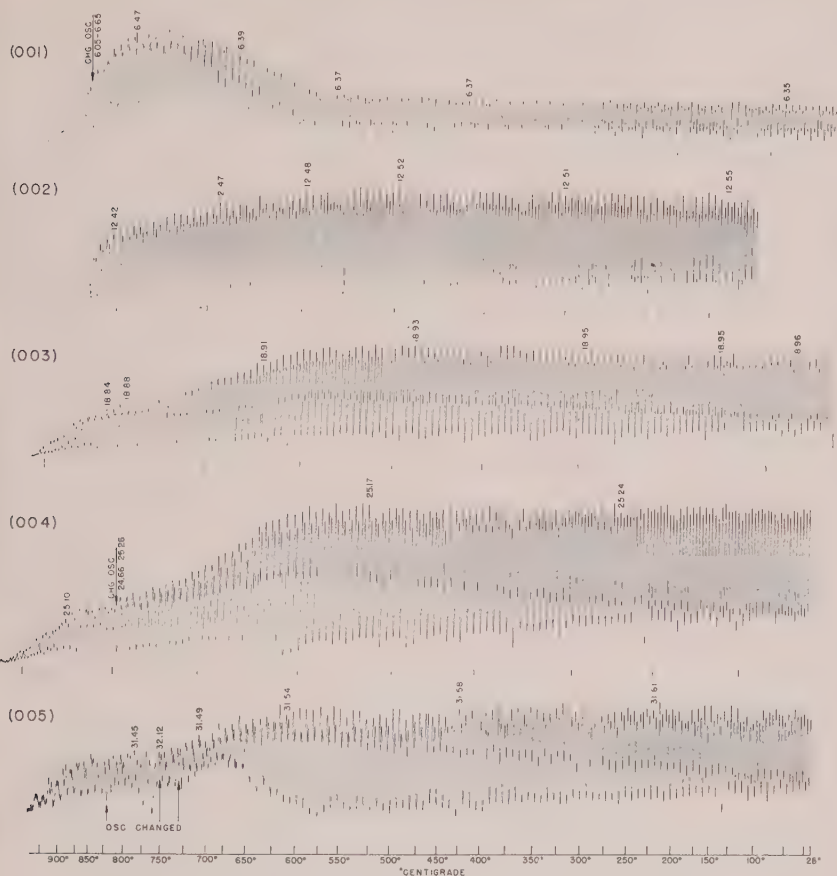


FIG. 5. Heating-oscillation patterns of the first five orders of the basal spacing of a Vermont chlorite.

imum. At this temperature the  $14 \text{ \AA}$  (001) maximum is most intense. The abrupt collapse of these three maxima is characteristic of clinochlore.

The oscillation tracing of the (004) basal diffraction maximum shows a shift toward a smaller spacing and collapse at  $575^\circ \text{ C.}$  and  $24.9^\circ 2\theta$ . The behavior of the (005) basal diffraction maximum is similar to that of the (004). However a new maximum, formed at  $570^\circ \text{ C.}$ , which persists to  $900^\circ \text{ C.}$ , may be the result of the formation of olivine.

*Vermont Chlorite.* The oscillation tracings of the first, second, third, fourth and fifth orders of the (00 $l$ ) basal maxima of a Vermont chlorite are shown in Fig. 5.

The (001) maximum begins a gradual increase in intensity at  $600^\circ \text{ C.}$  which attains its greatest height at  $780^\circ \text{ C.}$  It then decreases uniformly

until its disappearance at  $910^{\circ}\text{C}$ . There is a shift toward a smaller spacing from  $600^{\circ}\text{C}$ . to  $910^{\circ}\text{C}$ .

The (002) maximum, which shifts slightly toward a larger spacing, begins a gradual decrease in intensity at  $600^{\circ}\text{C}$ ., then the intensity decrease becomes more rapid at  $580^{\circ}\text{C}$ . At  $680^{\circ}\text{C}$ ., the intensity decrease again becomes gradual and continues until the maximum disappears above  $910^{\circ}\text{C}$ .

The oscillation tracing of the (003) maximum indicates an almost constant spacing ( $18.95^{\circ} 2\theta$ ) up to  $600^{\circ}\text{C}$ ., after which there is shift to a larger spacing ( $18.84^{\circ} 2\theta$ ). The gradual decline and disappearance of this maximum then follows the behavior of the (002) maximum.

The oscillation tracings of the (004) and (005) maxima shift slightly toward a larger spacing. The (004) from  $25.25^{\circ} 2\theta$  to  $25.17^{\circ} 2\theta$  and the (005) from  $31.61^{\circ} 2\theta$  to  $31.54^{\circ} 2\theta$ . The initial break in intensity for each is at  $600^{\circ}\text{C}$ . On the (004) oscillation tracing, there is an indication of the development of a new maximum at  $750^{\circ}\text{C}$ . At the same temperature a definite new maximum at  $32.1^{\circ} 2\theta$  is developed on the (005) oscillation tracing. Both of these maxima disappear near  $800^{\circ}\text{C}$ . Above  $800^{\circ}\text{C}$ ., another maximum at  $31.25^{\circ} 2\theta$  becomes evident on the (005) oscillation tracing. This may be attributed to the development of olivine.

### CONCLUSIONS

A composite drawing of a room temperature chlorite diffraction pattern and the outline of the heating-oscillation tracings for clinochlore and chlorite is shown in Fig. 6. The differences between these two chlorites may be summarized as follows:

1. The increase in intensity of the (001) maximum for the clinochlore is greater and more abrupt than that of the Vermont chlorite.

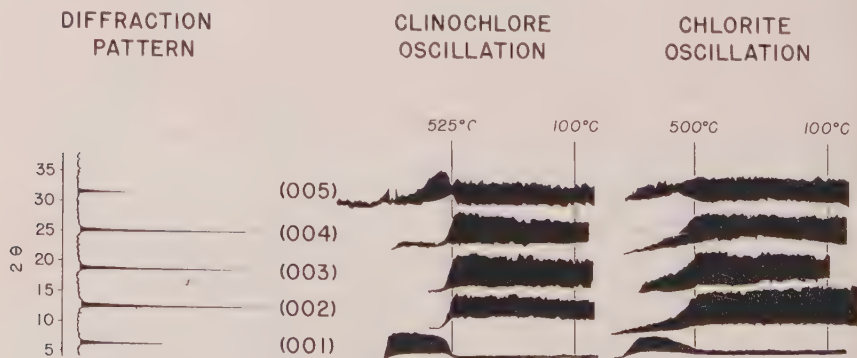


FIG. 6. Composite heating-oscillating pattern envelopes comparing the first five orders of the basal spacing of a clinochlore and a chlorite.



2. The (002), (003) and the original (004) and (005) maxima of the clinochlore collapse completely prior to the temperature of collapse of the (001) maximum.

3. At the temperature of the increase in intensity of the (001) maximum, all other basal diffraction maxima of the Vermont chlorite collapse only partially. The final collapse of all orders takes place at approximately the same temperature.

4. The intensity of the clinochlore maxima rises and decreases abruptly in contrast to the gradual rise and decrease in intensity of the Vermont chlorite.

5. The spacing shifts are greater for the Vermont chlorite than for the clinochlore. The collapse of the second, third, fourth, and fifth orders of the (00 $l$ ) basal diffraction maxima of clinochlore occurs at a temperature below the temperature of collapse of the first order (001) basal diffraction maximum. The collapse of the first five (00 $l$ ) basal orders of the Vermont chlorite takes place at the same temperature. Further distinctions may be made with regard to the amount of the decrease in intensity of the (002) maximum and the amount of increase in intensity of the (001) maximum. These may be seen by comparing the (002) oscillation and heating pattern of sheridanite, Fig. 3, and Vermont chlorite, Fig. 5.

The differences in the heating records of the different chlorite specimens may be explained on the basis of differences in their chemical compositions. It was established by Brindley and Ali<sup>5</sup> that the major factor in intensity alterations following heat treatments of chlorites was the expulsion of water from the brucite layer, with consequent rearrangement of the non-volatile brucite layer remnants. Structural formulae indicate that for complete dehydration water would be lost from the brucite layer and from the talc layer in the ratio of 3 mols to 1. The actual ratio may well be much higher, but could hardly be lower.

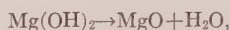
Augmented intensity in the first order is a consequence of the heat treatment having made the brucite layer differ from the brucite member of the talc layer by more than was the case before heating. The big factor is water loss, and any rearrangement is relatively ineffective.

Decline in intensity of the second order does not distinguish whether the reaction which took place was effective in the brucite layer, in the brucite member of the talc layer, or both. The decline only measures the magnitude of the reaction, and both water loss and rearrangement are effective in bringing the decline about. In a sense, a chlorite is a double-

<sup>5</sup> Brindley, G. W., and Ali, S. Z., Thermal Transformations in Magnesian Chlorites: *Acta Cryst.*, **3**, 25-30 (1950).

unit structure, so that the responses of the even orders measure the reaction, and those of the odd orders locate it.

For the high magnesian compositions, the local reaction may be represented schematically as



in which event  $\frac{1}{2}$  of the oxygen of the brucite layer is expelled. For compositions high in ferrous iron, roasting also oxidizes the iron. The comparable reaction, written as



illustrates that only  $\frac{1}{4}$  of the brucite layer oxygen is lost from the solid product. The same proportion obtains for the oxidized chlorites.

The lesser increase in 001 intensity for iron-bearing species is a reflection of this lesser loss of oxygen from the structure, and the lesser decline in 002 intensity indicates that the rearrangement which characterizes magnesian members is also inhibited.

Additional factors may be operative in modification of many chlorites by heat, particularly in instances in which some brucite layers are so abnormally hydrous that they collapse locally to talc in the course of the heating. Such collapse does not appear to have been extensive in these present instances.

The distinction and subgrouping of various definite types of chlorite is facilitated by the detailed information available from the oscillation-heating x-ray diffraction technique. The characteristics and differences among the three chlorites and the kaolinite which have been discussed are based upon an investigation by the oscillation-heating technique of many micaceous materials. The materials include montmorillonites, vermiculites and mixed-layer minerals in addition to chlorite and kaolinite.

#### ACKNOWLEDGMENTS

The assistance of W. F. Bradley, J. F. Burst and G. D. Brunton in the development and perfection of this technique and in the interpretation of the results is gratefully acknowledged.

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# STUDIES OF URANIUM MINERALS (XIX): RUTHERFORDINE, DIDERICHITE, AND CLARKEITE<sup>1,2</sup>

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## ABSTRACT

Rutherfordine, diderichite, and a synthetic uranyl carbonate obtained by heating  $\text{UO}_3$  in  $\text{H}_2\text{O}$  under 15,000 psi  $\text{CO}_2$  at  $300^\circ\text{C}$ . afforded identical x-ray powder patterns, and on analysis each yielded the formula  $(\text{UO}_2)(\text{CO}_3)$ . The name rutherfordine has priority. Two new localities are recorded for rutherfordine at Beryl Mountain, N. H., and Newry, Maine, where it occurs as a weathering product of uraninite in pegmatite. Rutherfordine occurs as crusts and aggregates of orthorhombic (?) fibers; biaxial positive, with  $nX=1.720$ – $1.723$ ,  $nY=1.728$ – $1.730$ ,  $nZ=1.755$ – $1.760$ ;  $Y$  along the fiber length.

Clarkeite is described from its second known locality, the Ajmer district, Rajputana, India, where it occurs as microcrystalline, chocolate-brown alteration product of uraninite in pegmatite. Analysis yielded the formula  $(\text{Na}, \text{Ca}, \text{Pb}, \text{Th}, \text{H}_2\text{O})_2\text{U}_2(\text{O}, \text{H}_2\text{O})_7$ ; isostructural with  $\text{Na}_2\text{U}_2\text{O}_7$  and  $\text{CaU}_2\text{O}_7$ . Specific gravity is 6.29, mean index of refraction 1.94–1.97.

## RUTHERFORDINE

Four supposedly distinct uranyl carbonates have been described: rutherfordine, diderichite, sharpite, and studtite. The scant existing data for these minerals, summarized in Table 1, make further study desirable. About 20 specimens labeled rutherfordine from the original locality at Morogoro, Tanganyika, Africa, were available for study. Most of these specimens were found to consist variously of kasolite, uranophane, and hydrated lead uranyl oxides as alteration zones about cubes of uraninite, and only two contained a uranyl carbonate. The latter mineral was earthy to pulverulent in consistency, with a pale brownish-yellow to straw-yellow color and dull luster. Under the microscope the mineral appeared as minute fibers and lathlike subparallel aggregates: biaxial positive, with  $nX=1.723$  (nearly colorless),  $nY=1.730$  (pale yellow),  $nZ=1.760$  (pale greenish yellow); extinction parallel, with  $Y$  along the elongation and  $Z$  perpendicular to the flattening. The mineral probably is orthorhombic. A new chemical analysis, made on material known to contain a small amount of kasolite, is close to the original analysis of Marckwald (1906). Both analyses, cited in Table 2, have been recalculated after deducting the Pb and Ca, as kasolite and uranophane, together with the  $\text{H}_2\text{O}^-$ , iron oxide, and residual Si or Ca.

<sup>1</sup> Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 360.

<sup>2</sup> Publication authorized by the Director, U. S. Geological Survey.

TABLE 1. DATA SUMMARIZED FROM THE LITERATURE ON THE  
NATURAL URANYL CARBONATES

	Rutherfordine	Diderichite	Sharpite	Studite
Symmetry	Orthorhombic?	Orthorhombic?	Orthorhombic?	Orthorhombic?
Habit	Aggregates of minute fibers	Fibrous crusts	Fibrous crusts	Fibrous crusts
Composition	$(\text{UO}_2)(\text{CO}_3)?$	Slightly hydrated uranyl carbonate	$(\text{UO}_2)(\text{CO}_3) \cdot \text{H}_2\text{O}?$	Hydrated uranyl carbonate with Pb
Analysis	Cited by Marckwald (1906)	Qualitative tests only	Cited by Mélon (1938)	Qualitative tests only
Color	Yellow	Yellow-green	Greenish yellow	Yellow
Specific gravity	4.82?	—	3.33	—
Indices of refraction	$n_X = 1.72 \pm 0.01$ $n_Y = \text{—}$ $n_Z = 1.80 \pm 0.01$	1.722–1.728 1.728 1.728–1.74	1.633, brownish — 1.72, greenish yellow	1.545 1.555 1.68
Other optic data		$Y = \text{elong.}$ Biaxial positive 2V large	$Z = \text{elong.}$ $Y \perp \text{flattening}$	$Z = \text{elong.}$ Biaxial negative 2V large
Thermal data	$\text{CO}_2$ lost over 300° C.		$\text{H}_2\text{O}$ lost 200–275° C. $\text{CO}_2$ and $\text{H}_2\text{O}$ at 325° C.	
Locality	Morogoro, Tanganyika	Katanga, Belgian Congo	Katanga, Belgian Congo	Katanga, Belgian Congo
References	Marckwald (1906) Larsen (1921)	Vaes (1947)	Mélon (1938)	Vaes (1947)

The ratios then are close to the formula  $(\text{UO}_2)(\text{CO}_3)$ , originally given for this mineral by Marckwald (1906) and later accepted by Mélon (1938) and others.

The x-ray powder spacing data are given in Table 3. These data are virtually identical with those given by Miller, Pray, and Munger (1949) for synthetic  $(\text{UO}_2)(\text{CO}_3)$ , and are identical with those afforded by a product<sup>3</sup> obtained by heating precipitated  $\text{UO}_3 \cdot n\text{H}_2\text{O}$  at 300° C. under 15,000 psi  $\text{CO}_2$ . An analysis of the latter substance, given in Table 2, affords the formula  $(\text{UO}_2)(\text{CO}_3)$ . This material was found to contain a small amount of  $\text{U}_3\text{O}_8$  formed by thermal dissociation of the  $\text{UO}_3$ , accounting for the  $\text{UO}_2$  reported in the analysis, together with a small amount of an unidentified impurity. The particle size of the material was too small for satisfactory optical study. It may be noted that the analyses of the natural and synthetic substances (Table 2) all show a small amount of water retained over 110° C. Although our data for rutherfordine are not based on a type specimen, the close correspondence in physical and chemical properties with the original description leaves little doubt but that they are representative of the mineral. The only discrepancy is with the description of a non-type specimen by Larsen

<sup>3</sup> Prepared for us by Miss E. Berman and Dr. G. Kennedy, Harvard University, 1953.

TABLE 2. CHEMICAL ANALYSES OF URANYL CARBONATES

	1	2	3	4	5	6	7	8
UO <sub>3</sub>	86.68	86.7	85.9	86.6	87.7	83.8	78.6	85.5
UO <sub>2</sub>								2.6
CaO						1.1	0.2	
PbO						1.0	4.2	
Fe <sub>2</sub> O <sub>3</sub>						0.8	1.1	
SiO <sub>2</sub>						0.8	1.8	
H <sub>2</sub> O+		0.2	1.4	n.d.	0.5	0.7	1.9	0.5
H <sub>2</sub> O—							0.6	0.0
CO <sub>2</sub>	13.32	13.1	12.7	13.6	11.8	12.1	10.5	11.2
Total	100.00	100.0	100.0	100.2	100.0	100.3	98.9	99.8
Specific gravity			5.8	5.43	6.10		5.08	6.10

1. Theoretical weight percentages, (UO<sub>2</sub>)(CO<sub>3</sub>).
2. Rutherfordine, Morogoro. Original analysis of Marckwald (1906), column 6, recalculated to 100 after deduction of Pb and Ca as kasolite and uranophane together with remaining CaO and FeO.
3. Rutherfordine, Morogoro. New analysis of R. Meyrowitz (column 7), recalculated after deduction of Pb and Ca as kasolite and uranophane together with remaining SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O—.
4. Diderichite, Katanga. Analyst: R. Meyrowitz, 1954. Type material of Vaes. Contains a small but undetermined amount of H<sub>2</sub>O.
5. Synthetic uranyl carbonate. Recalculated from the analysis of Meyrowitz (column 8) after deduction of UO<sub>2</sub> as U<sub>3</sub>O<sub>8</sub>.
6. Rutherfordine, Morogoro. Original analysis of Marckwald (1906). Fe reported as FeO.
7. Rutherfordine, Morogoro. Analyst: R. Meyrowitz, 1954. Known to contain some admixed kasolite.
8. Synthetic uranyl carbonate. Analyst: R. Meyrowitz, 1954. Known to contain some admixed U<sub>3</sub>O<sub>8</sub>.

TABLE 3. X-RAY POWDER DIFFRACTION SPACING DATA FOR RUTHERFORDINE

(CuK $\alpha$ /Ni)

<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)
10	4.60	2	2.41	2	1.874	2	1.435
8	4.29	3	2.32	3	1.734	3	1.388
6	3.90	4	2.15	1	1.658	1	1.373
9	3.21	5	2.05	1	1.603	1	1.346
4	2.64	1	1.95	1	1.588	1	1.318
1	2.51	2	1.914	2	1.510	1	1.275



(1921, p. 129), cited in Table 1. His value  $nX$  1.72 agrees with ours, but his  $nZ$  1.80 is much higher and probably was obtained on an admixed uranium oxide.

We have identified rutherfordine on the basis of  $x$ -ray patterns and qualitative chemical tests from two additional localities. It occurs abundantly at Beryl Mountain, N. H., as dense to earthy pseudomorphs after uraninite in pegmatite, associated with schoepite, vandendriescheite, and uranophane. It also occurs as an alteration of uraninite at Newry, Maine. At both localities the mineral forms earthy, yellow to straw-yellow aggregates of extremely small particle size, and appears to be a weathering product. Certain specimens of yellow to orange "gum-mite" from the Ruggles and Palermo pegmatites, both in New Hampshire, also were found to effervesce slightly in dilute HCl, but rutherfordine could not be identified in them with certainty.

Rutherfordine, synthetic  $(\text{UO}_2)(\text{CO}_3)$  and diderichite (see beyond) were not observed to fluoresce under either short- or long-wave ultraviolet radiation. This conflicts with the observation of Bültemann (1954), who found rutherfordine from Morogoro to fluoresce strongly in yellow-green.

#### DIDERICHITE

An authentic specimen of diderichite from the type locality at Katanga, Belgian Congo, was kindly given to us by Dr. J. F. Vaes, of the Union Minière du Haut Katanga, who described the mineral in 1947. The  $x$ -ray powder pattern proved to be identical with that of rutherfordine and a chemical analysis, cited in Table 2, is very close to the formula  $(\text{UO}_2)(\text{CO}_3)$ . The mineral occurs as crusts of fibers and laths. These are biaxial positive, with  $nX=1.720$  (pale yellow),  $nY=1.728$  (yellow),  $nZ=1.755$  (greenish yellow), with  $2V$  large. They also have parallel extinction, with  $Y$  along the elongation and  $Z$  perpendicular to the flattening. These data agree with those of Vaes (1947) and with our data for rutherfordine. We consider that diderichite is identical with rutherfordine. The latter name has priority.

#### SHARPITE AND STUDTITE

No new data have been obtained for either sharpite or studtite. The type specimens of sharpite were destroyed during the Second World War,<sup>4</sup> and other specimens do not appear to be extant. A specimen labeled studtite from the type locality at Katanga was available for study, but despite careful examination no mineral closely answering the

<sup>4</sup> Private communication, Professor H. Brasseur, University of Liège, 1954.

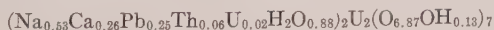
description of this species was found on it. The optical properties of both sharpite and studtite, cited in Table 1, are distinct from those of rutherfordine and the other known carbonates of uranium.

#### CLARKEITE

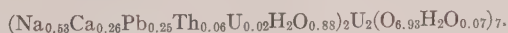
Clarkeite, hitherto known only from the Spruce Pine district, N. C., has been identified as an alteration product of uraninite in pegmatite in the Ajmer district, Rajputana, India. The specimens, striking in appearance, consist of fractured and in part kaolinized masses of white feldspar containing crystals of uraninite as much as an inch in diameter. The uraninite crystals are zonally altered, and show a small, embayed core of black uraninite, a surrounding zone of deep chocolate-brown clarkeite with a waxy luster, a succeeding zone of bright orange-red microcrystalline fourmarierite, and an outer pale yellowish-green zone composed chiefly of uranophane. In some specimens the residual core of uraninite is lacking, and in others the crystals have been completely altered to uranophane. A zoned specimen from Rajputana apparently of this nature is mentioned by Krishnan (1948), and details of the uraninite from this region are given by Crookshank (1948).

The clarkeite is dense and microcrystalline. The color in transmitted light is deep brownish yellow, the mean index of refraction, slightly variable, is between 1.94 and 1.97, and the specific gravity is 6.29. The x-ray powder pattern is virtually identical with that obtained from the analysis sample of the original material from Spruce Pine described by Ross, Henderson, and Posnjak (1931). X-ray powder data for the latter mineral and for synthetic clarkeite are given by Gruner (1954).

A chemical analysis of the Rajputana material is cited in Table 4. The analysis is close to the ratio  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{PbO} \cdot 8\text{UO}_3 \cdot 6\text{H}_2\text{O}$ . Gruner (1954), however, has shown that clarkeite is a diuranate isostructural with  $\text{Na}_2\text{U}_2\text{O}_7$  and  $\text{CaU}_2\text{O}_7$ . Water is present in the natural material and in some synthetic preparations but is not essential to the structure. Both the Rajputana and Spruce Pine materials are solid solutions between  $\text{Na}_2\text{U}_2\text{O}_7$ ,  $\text{CaU}_2\text{O}_7$ , and  $\text{PbU}_2\text{O}_7$  in which the cation vacancies are occupied by neutral  $\text{H}_2\text{O}$  molecules and in which valence compensation is effected by a concomitant substitution of (OH) or  $\text{H}_2\text{O}$  for O. Our analysis of the Rajputana material conforms to the formula



or to



The calculated weight percentages for the latter formula are given in Table 4.

TABLE 4. CHEMICAL ANALYSIS OF CLARKEITE FROM RAJPUTANA

	1	2	3
Na <sub>2</sub> O	2.4	2.3	2.3
CaO	2.1	2.1	2.1
PbO	8.0	8.0	7.9
UO <sub>2</sub>	0.8	0.8	0.8
UO <sub>3</sub>	82.0	80.2	79.9
ThO <sub>2</sub>	2.3	2.4	2.4
H <sub>2</sub> O+	2.4	4.2	4.2
H <sub>2</sub> O—			1.3
Insol.			0.2
Total	100.00	100.0	101.1
Specific gravity			6.29

1. Theoretical weight percentages for the derived formula (Na<sub>0.55</sub>Ca<sub>0.26</sub>Pb<sub>0.25</sub>Th<sub>0.06</sub>U<sub>0.02</sub>H<sub>2</sub>O<sub>0.88</sub>)<sub>2</sub>U<sub>2</sub>(O<sub>6.93</sub>H<sub>2</sub>O<sub>0.07</sub>)<sub>7</sub>.

2. Analysis 3 recalculated to 100 after deduction of insoluble and H<sub>2</sub>O—.

3. Clarkeite, Rajputana. Analyst: R. Meyrowitz, 1953.

The above interpretation may have to be modified in light of work by Wamser et al. (1952), who indicate that the supposed compound Na<sub>2</sub>U<sub>2</sub>O<sub>7</sub> actually has the composition Na<sub>6</sub>U<sub>7</sub>O<sub>24</sub>. They find that air dried material contains 16H<sub>2</sub>O and that there is no change in x-ray pattern when the water is completely driven off by heating to 130°.

#### ANALYTICAL METHODS

The methods employed were guided by semiquantitative spectrographic analyses of the samples by C. S. Ansell, U. S. Geological Survey. Quadrivalent uranium was determined by dissolving the mineral in 1:3 H<sub>2</sub>SO<sub>4</sub> and titrating with approximately 0.03 N potassium permanganate that had been standardized against a known uranium solution. Sexivalent uranium was calculated by difference after total uranium had been determined by reduction in a Jones reductor and titrating with standard potassium permanganate, using the same sample employed for the determination of quadrivalent uranium; lead was removed as the sulfate prior to the reduction of the dilute solution. The alkaline earths were determined as the sulfates after separation as the sulfates from a 85 per cent ethyl alcohol solution. The alkalis were determined as the sulfates; the alkali pyrosulfate formed on ignition was converted to the normal sulfate by heating with successive small samples of ammonium carbonate in a covered dish to constant weight. Lead was separated as the sulfide and determined as the sulfate. The R<sub>2</sub>O<sub>3</sub> group was precipitated by CO<sub>2</sub> free ammonium hydroxide. Qualitative spectrographic analyses were made of the total alkali, total alkaline earth, and total R<sub>2</sub>O<sub>3</sub> precipitates. In the carbonate analyses, the CO<sub>2</sub> and H<sub>2</sub>O were determined by a modified microcombustion train of the type used for determination of C and H in organic compounds. The samples were decomposed by ignition at 900° C. in a stream of oxygen. In the clarkite analyses the H<sub>2</sub>O was calculated from the loss on ignition. H<sub>2</sub>O— was determined by dehydrating the sample to constant weight at 110° C. The iron was determined using o-phenanthroline. A standard iron curve was prepared using solutions that

contained approximately the same amount of uranium contained in the aliquot of solution used for the determination of iron. The thorium was calculated by difference using the  $R_2O_3$  value. The samples employed in the separate determinations ranged in weight from 20 to 100 mg.

This work was supported in part by the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

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## THE EMPIRICAL UNIT-CELL CONTENTS OF THE FRIEDELITE FAMILY

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Fron del and Bauer (1953) have shown that the friedelite family of minerals can be divided into three sections: pyrosmalite and mangan-pyrosmalite, with  $c=7.15 \text{ \AA}$ ; schallerite, with  $c\approx 14.3 \text{ \AA}$  (both Type I with  $\text{As}_2\text{O}_3\approx 12\%$  and Type II with  $\text{As}_2\text{O}_3\approx 6$  to  $8\%$ ); and friedelite and ferroschallerite with  $c=21.43 \text{ \AA}$ . Taking one analysis of manganpyrosmalite, they calculated the empirical unit-cell contents included (with a small correction) in Table 1 below (column 1); these clearly indicate a unit-cell formula  $[(\text{Mn}, \text{Fe}, \text{Mg}, \text{Zn})_{16}\text{Si}_{12}\text{O}_{30}(\text{OH}, \text{Cl})_{20}]$ , neglecting the As, too small in amount to locate. Noting the simple multiple relation in their cell-dimensions, they concluded that the unit-cell contents of pyrosmalite, schallerite, and friedelite (including ferroschallerite, regarded as an arseniferous variety of friedelite) are respectively:  $2[(\text{Mn}, \text{Fe})_8\text{Si}_6\text{O}_{15}(\text{OH}, \text{Cl})_{10}]$ ,  $4[(\text{Mn}, \text{Fe})_8(\text{Si}, \text{As})_6\text{O}_{15}(\text{OH}, \text{Cl})_{10}]$ , and  $6[(\text{Mn}, \text{Fe})_8(\text{Si}, \text{As})_6\text{O}_{15}(\text{OH}, \text{Cl})_{10}]$ .

McConnell (1954) made an independent study of schallerite; for Type II material with  $\text{As}_2\text{O}_3$  6.37% he found a unit-cell 0.5% smaller along both  $a$ - and  $c$ -axes than Fron del and Bauer had found, probably for Type I schallerite. From Fron del and Bauer's cell-dimensions and the density and chemical analysis of Bauer and Berman (1928), he calculated a unit-cell content of 105.2 (O, OH, Cl), and taking this as an approximation to an integral 104 (supported by the fact that the absence of odd orders of (000) diffractions indicates that the space-group contains only even numbers of lattice positions), he recalculated the analysis to a basis of 104 (O, OH, Cl). This gave  $(\text{Mn}, \text{Fe}, \text{Mg}, \text{Ca})_{32.5}\text{As}_{5.5}\text{Si}_{23.5}\text{O}_{71.4}(\text{OH})_{32.6}$  or nearly  $4[(\text{Mn}, \text{Mg}, \text{Fe})_8\text{As}_{1.1}\text{Si}_6\text{O}_{18}(\text{OH})_8]$  for schallerite. McConnell further concluded that the formulae of pyrosmalite and friedelite are probably  $2[(\text{Mn}, \text{Mg}, \text{Fe})_8\text{Si}_6\text{O}_{14}(\text{OH}, \text{Cl})_{12}]$  and  $6[(\text{Mn}, \text{Fe}, \text{Mg})_8\text{Si}_6\text{O}_{14}(\text{OH}, \text{Cl})_{12}]$  respectively.

Though Fron del and Bauer only considered one analysis of pyrosmalite, their deduction of the formula of pyrosmalite is perfectly sound; but their assumption that, because schallerite and friedelite have respectively twice and three times the cell-volume of pyrosmalite, their formulae must be simply twice and three times the pyrosmalite formula (apart from some replacement of Si by As in schallerite) is quite unsound; and equally, McConnell's reverse assumption that the formulae of pyrosmalite and friedelite may be deduced from that of schallerite is unsound.

The only strictly reliable and convincing evidence of true unit-cell



TABLE 1. EMPIRICAL UNIT-CELL CONTENTS OF MANGANPYROSMALITE, PYROSMALITE, SCHALLERITE, FRIEDELITE, AND FERROSCHALLERITE

	1*	2	3	4	5	6*	7*	8*
Si	11.9	12.6	12.0	12.0	12.1	24.1	23.5	23.9
As	0.02	—	—	—	—	5.6	5.6	3.4
(Mn, Fe, etc.)	16.0	15.5	15.8	16.1	17.3	32.3	32.6	33.2
(OH, Cl)	21.2	20.7	22.0	18.7	22.4	35.6	32.7	36.4
O	29.3	30.4	27.8	30.7	30.3	71.1	71.6	69.1
Σ(cations)	27.9	28.1	27.8	28.1	29.4	62.0	61.7	60.5
Σ(O, OH, Cl)	50.5	51.0	50.8	49.4	52.8	106.6	104.3	105.5
<hr/>								
	6a	7a	8a	9	10	11	12	
Si	23.7	23.1	24.3	35.4	33.8	35.4	33.8	
As	5.5	5.5	3.4	—	—	—	—	
(Mn, Fe, etc.)	31.8	32.1	33.8	47.1	48.1	47.8	50.8	
(OH, Cl)	35.0	32.2	36.9	71.6	64.2	64.7	56.7	
O	70.0	70.5	70.2	82.1	83.5	86.3	90.1	
Σ(cations)	61.0	60.7	61.5	82.5	81.9	83.2	84.6	
Σ(O, OH, Cl)	105.0	102.7	107.1	153.7	147.7	151.0	146.8	
<hr/>								
	13	14	14a	15*	16*	17*	17a	
Si	33.5	37.7	35.7	34.7	35.1	35.7	23.8	
As	—	—	—	0.7	—	8.7	5.8	
(Mn, Fe, etc.)	52.6	48.5	45.8	47.1	45.3	48.1	32.1	
(OH, Cl)	54.4	69.6	65.8	68.0	67.1	49.2	32.8	
O	92.5	89.1	84.2	83.6	81.9	108.1	72.0	
Σ(cations)	86.2	86.2	81.5	82.6	80.4	92.6	61.7	
Σ(O, OH, Cl)	146.9	158.7	[150]	151.7	149.0	157.3	104.8	

\* Material studied by Frondel and Bauer by X-ray methods.

*Manganpyrosmalite:*

1. Sterling Hill, N.J. C. Frondel and L. H. Bauer, *Am. Mineral.*, 1953, **38**, 755; the oxygen value of 2.3591 cited in table 2, p. 757 is incorrect, as the oxygen equivalent of the chlorine has not been subtracted, nor the oxygen of the  $\text{As}_2\text{O}_3$  added in; with these corrections, Frondel and Bauer's data yield the figures tabulated here.

*Pyrosmalite:*

2. Nordmark, Sweden. J. Lang, *Jour. prakt. Chem.*, **83**, 424 (1861).
3. Nordmark, Sweden. E. Ludwig, *Tscherm. Min. Mitt.*, 211 (1875).
4. Dannemora, Sweden. N. Engström, *Geol. För. Förhändl., Stockholm*, **3**, 116 (1876).
5. Dannemora, Sweden. A. Gorgeu, *Bull. Soc. Min. France*, **7**, 58 (1884); the cited density (3.19) is probably too high; the mineral was closely associated with hedenbergite.

TABLE 1—(continued)

*Schallerite:*

6. Franklin, N.J.; (type I). R. B. Gage, E. S. Larsen, and H. E. Vasser, *Am. Mineral.*, **10**, 9 (1925); re-calculated assuming the As is all trivalent, and with Frondel and Bauer's cell-dimensions.
7. Franklin, N.J.; (type I). L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 342 (1928), table 1, No. 7, and table 2a, No. 4; re-analysis of type material; calculated using Frondel and Bauer's cell-dimensions.
8. Franklin, N.J.; (type II). L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 342 (1928), table 1, No. 9, and table 2a, No. 3; calculated using McConnell's cell-dimensions.
- 6a. } Re-calculation of analysis 6, 7, and 8, using McConnell's cell-dimensions for
- 7a. } analyses 6 and 7, and Frondel and Bauer's for analysis 8.
- 8a. }

*Friedelite:*

9. Adervielle, Neste de Louron, Hautes Pyrenées. E. Bertrand (A. Gorgeu, analyst), *Bull. Soc. Min. France*, **7**, 3 (1884).
10. Harstig mine, Wermland, Sweden. G. Lindström, *Geol. För. Förhandl., Stockholm*, **13**, 127 (1891).
11. Harstig mine, Wermland, Sweden. G. Flink, *Bihang. Sver. Vet.-Akad. Handl.*, **16**, part 2, No. 4 (1890).
12. } Veitsch, Styria. A. Hofmann and F. Slavík (F. Kovář, analyst), *Rozpr. České*
13. } *Akad.*, Ser. II, **18**, No. 27 (1909).
14. Vielle-Aure, Neste d'Aure, Hautes Pyrenées. H. Lienau, [*Chem.-Zeitung*, **1**, 362 (1905)] quoted by C. Doelter, *Handb. Min. Chem.*, **2**, part I, 749 (1914) with an incorrect locality; correct locality see Dana, *Syst. Min.*, 6th edn, App II, p. 43; the cited density (3.21) is probably too high.
- 14a. Analysis 14 re-calculated on a basis of 150 (O, OH, Cl).
15. Franklin, N.J. C. Palache (W. T. Schaller, analyst), *Am. Jour. Sci.*, ser. 3, **29**, 177 (1910); *Zeits. Kryst.*, **47**, 582 (1910); L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 341 (1928), table 1, No. 3, and table 2a, No. 1.
16. Franklin, N.J. L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 341 (1928), table 1, No. 4, and table 2a, No. 2.

*Ferroschallerite:*

17. Franklin, N.J. L. H. Bauer and H. Berman, *Am. Mineral.*, **15**, 340 (1930).
- 17a. Two-thirds the unit-cell contents of analysis 17, for comparison with analyses 6, 7, and 8.

NOTE: There are several analyses of members of the friedelite family in the literature which, being without density determinations, are useless for the calculation of empirical cell-contents.

contents comes from chemical analysis, density, and unit-cell dimensions, all determined on the same specimen. From these data the unit-cell contents and chemical formula may be derived by several procedures, including Frondel and Bauer's, McConnell's, and Hey's (1939, 1954); compare also Nicholls and Zussman (1955) and Francis and Hey (1956). Strictly, then, only analyses for which the unit-cell dimensions and the density were determined on the analysed material are valid data for the

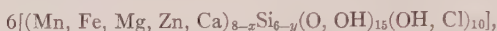
calculation of empirical unit-cell contents; but in many minerals, there is evidence that the range of variation of the unit-cell dimensions is limited, and it may then be reasonable to accept and use unit-cell dimensions determined on a different specimen, while allowing an increased assessment of probable error. Frondel and Bauer's *x*-ray data were obtained on material which included type specimens of schallerite, ferroschallerite, and manganpyrosmalite, and pyrosmalite from the original locality, Nordmark, Sweden. The difference in cell-dimensions between pyrosmalite and manganpyrosmalite is very small (0.01 Å in both *a* and *c*), and we may therefore reasonably use these cell-dimensions to calculate empirical unit-cell contents for all pyrosmalites for which densities and chemical analyses are available. Frondel and Bauer examined both Type I and Type II schallerite, but do not note any difference in lattice dimensions. McConnell's *x*-ray data were obtained on Type II schallerite and indicate a distinctly smaller cell. Empirical unit-cell contents based both on Frondel and Bauer's measurements and on McConnell's are therefore included in Table 1. For friedelite and ferroschallerite, Frondel and Bauer's work suggests that there is little or no variation in cell-dimensions. In view of the usually preponderant effect of errors in the physical data on the empirical unit-cell contents (Hey, 1954), it is probably safe to assume that the figures given in Table 1 are within about 2% of the truth, except as mentioned below.

It will be seen from Table 1 that the evidence probably indicates a unit-cell content of  $2[(\text{Mn}, \text{Fe})_8\text{Si}_6\text{O}_{15}(\text{OH}, \text{Cl})_{10}]$  for pyrosmalite and manganpyrosmalite, as found by Frondel and Bauer.

For schallerite, the unit-cell probably contains  $104(\text{OH}, \text{Cl})$ , as found by McConnell; the arsenic-poor Type II material probably has the distinctly smaller cell found by McConnell; As does not appear to substitute for Si, and the repeat is perhaps best written  $4[(\text{Mn}, \text{Fe})_8\text{As}_{2-x}\text{Si}_6(\text{O}, \text{OH}, \text{Cl})_{26}]$ , where *x* is about 0.6 and *O*:(OH, Cl) varies, perhaps from about 2.2 to about 1.9; but more analyses, with *x*-ray and density data, will be necessary before the nature of the substitutions in this mineral is clear.

Eight analyses of friedelite are available, including two of material examined by *x*-ray methods by Frondel and Bauer (Table 1, columns 15 and 16); assuming that the cell-dimensions are constant, and using Frondel and Bauer's values, the unit-cell contents included in Table 1 are derived. One analysis (column 16) includes 1.94%  $\text{H}_2\text{O}$ —, but if this is assumed to be impurity, deducted from the analysis, and the density adjusted accordingly, the empirical unit-cell contents fall out of line with the other seven analyses, so it has been assumed that all the water in this analysis is essential. It seems fairly clear that the total (O, OH, Cl) is

150 atoms per unit cell in friederite, and that the high value for analysis 14 is simply due to a high (and incorrect) density. Analyses 12 and 13, which combine low (O, OH, Cl) with low (OH, Cl) and low Si, but high total cations, are probably analyses of impure material. The remaining analyses indicate a formula



where  $x$  and  $y$  can each reach about 0.3 and the deficit in valency is balanced by OH replacing O up to nearly 10(OH) per unit cell.

Ferroschallerite presents a difficult problem; Frondel and Bauer, noting that it has the 21 Å basal spacing and gives an x-ray powder photograph like that of friederite, concluded that it is merely an arsenic-rich variety of friederite; it cannot be classed as a variety of schallerite, which gives a distinct x-ray powder pattern and has a 14 Å basal spacing, yet its empirical unit-cell contents (Table 1, columns 17 and 17a) are quite distinct from those of friederite and approximate to  $1\frac{1}{2}$  times the unit-cell contents of schallerite. For the present, it seems best to regard ferroschallerite as a distinct species, with a unit-cell formula near



The apparent identity of the x-ray powder photographs is against ferroschallerite being a separate species, but there does not appear to be any authenticated example of a species showing a variation in unit-cell content comparable to that between friederite and ferroschallerite, while examples on non-isostructural species whose x-ray powder photographs are extremely similar are known (for example, gonnardite and natrolite; M. H. Hey, H. Meixner, and A. A. Moss, unpublished data).

The true relations of these four species remain somewhat obscure. The increase in oxygen atoms per unit-cell does not seem to bear any simple relation to the arsenic content. Indeed, both the arsenic-rich Type I schallerite and the arsenic-poor Type II appear to have the same total of anions (O, OH, Cl) per unit cell, which suggests that the relation is not an isomorphous replacement such as OH' by AsO<sub>2</sub>', as might seem possible.

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## NOTES AND NEWS

### A NOTABLE CENTENARY IN AMERICAN MINERALOGY: SAMUEL LEWIS PENFIELD, 1856-1906\*

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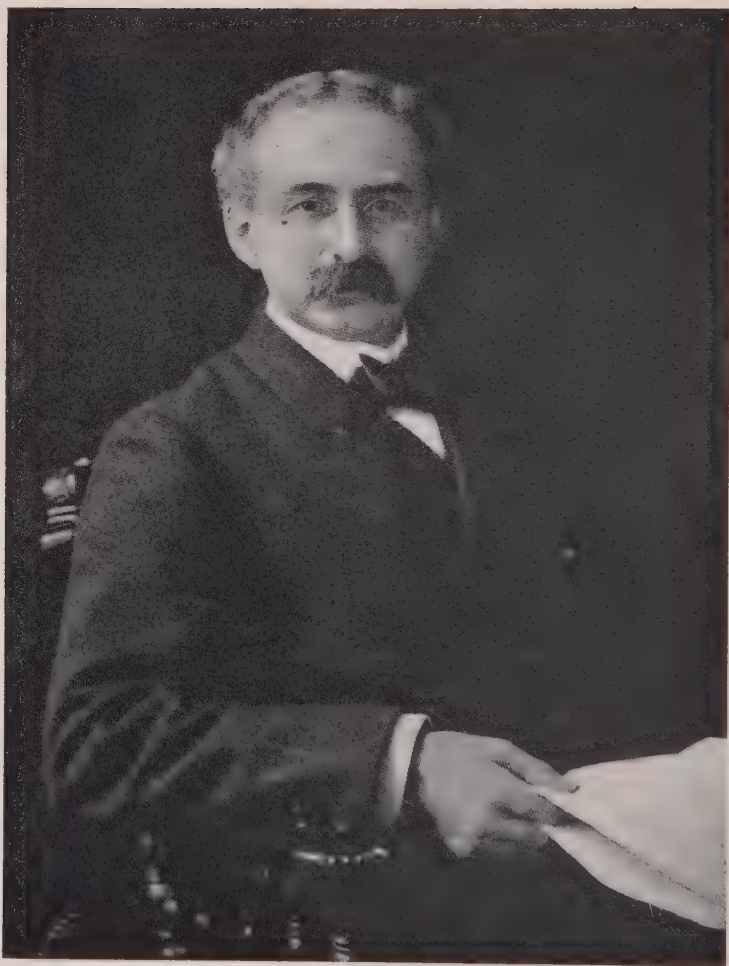
This year is the hundredth anniversary of the birth of one of the world's greatest mineralogists, Samuel Lewis Penfield, who was born January 16, 1856, at Catskill, N. Y., and died August 12, 1906, at South Woodstock, Conn. Despite the fact that his death after three years of illness with diabetes cut short his career when he was at the height of his ability, Penfield left a record of remarkable achievements. These had brought him fame and the esteem of his contemporaries. What is more remarkable, the passing of half a century has not dimmed their luster. It is not fair to judge work done fifty to eighty years ago by comparison with what we know today, but Penfield's work can stand such a comparison.

He was trained as a chemist and his early work consisted chiefly of mineral analyses. Penfield was a remarkable analyst. His colleague H. L. Wells wrote, "Difficult analyses always appeared to attract rather than to discourage him. He had perfect confidence in himself, was full of enthusiasm, and anxious to arrive quickly at his results; but at the same time he was exceedingly conscientious about his work, and this strict honesty led him to examine his methods and test his results so carefully that he never made poor analyses." In similar vein, J. P. Iddings wrote, "The uniformly high quality of his work is due to his absolute honesty and conscientiousness."

This conscientiousness is shown by Penfield's insistence on careful purification of every mineral he analyzed and on a full statement in each paper of just what purification procedure he used. He also described his methods of analysis and he often checked them by the analysis of material of known composition. Even so he was not always satisfied; for example, he published analyses of beryl in 1884, but two years later wrote that the separation of beryllium from aluminum had not been satisfactory and gave new determinations, with a warning, amply confirmed many years later, that the methods available were still unsatisfactory. Although few of Penfield's papers are concerned exclusively with analytical methods, he introduced many modifications of procedure that improved the speed and accuracy of inorganic analyses. A good example is his introduction in 1886 of the use of  $\text{NH}_4\text{NO}_3$  solution to wash precipi-

\* Publication authorized by the Director, U. S. Geological Survey.





*S. L. Penfield*

tates of hydrous aluminum oxides. Perhaps the best known of his methods is that proposed in his paper of 1894 on the determination of water; the simple, but accurate method he devised is still the most widely used to-day.

We usually think of microchemical analysis as a recent art, but Penfield in 1890 made an analysis of the complex mineral connellite on 74 milligrams. In 1898, he described how he tested a sample for sperrylite:

"The crystals, weighing in all 0.0019 gram, were roasted in an open tube and yielded a volatile sublimate of arsenious oxide, crystallizing in isometric octahedrons. The residue, after roasting, had the color of platinum and when dissolved in nitro-hydrochloric acid gave a yellow solution, which when tested with potassium chloride yielded isometric octahedrons of potassium platonic-chloride." In 1902, again faced with the problem of identifying sperrylite, he first measured the crystals, showing them to be pyritohedrons, then carried out the tests as above, this time on a sample weighing 0.0004 gram!

His skill and his care are perhaps best shown by the fact that he named 18 new minerals, every one a valid species, and with two exceptions mentioned below, the compositions established by him are accepted today. He described and named scovillite (1883), gerhardtite (1885), nesquehonite (1890), spangolite (1890), hamlinite (1890), canfieldite (1893, 1894), pearceite (1896), roeblingite (1897), bixbyite (1897), clinohedrite (1898), hancockite (1899), glaucochroite (1899), nasonite (1899), leuco-phoenicite (1899), graftonite (1900), natrojarosite (1902), plumbojarosite (1902), and tychite (1905). The names scovillite and hamlinite are not now used; scovillite, as Penfield himself showed, was identical with rhabdophane, described in England just before his paper naming scovillite appeared; hamlinite, described correctly by Penfield as a strontium aluminum phosphate, was shown 21 years later to be identical with goyazite, which had been described earlier as a calcium aluminum phosphate.

Later work has changed the formulas of only two of these minerals. Pearceite, given by Penfield as  $9 \text{ Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$ , is now considered to be  $8 \text{ Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$ . Roeblingite, described as a sulfite, was shown by Blix in 1931 to be a sulfate, as was confirmed by W. T. Schaller of the U. S. Geological Survey (private communication) on material from a tube in the Brush collection labelled in Penfield's handwriting. It is interesting that the late Professor H. W. Foote, who made the original analysis of roeblingite, could not believe in 1932, when we discussed the matter, that sulfite had not been present in the sample originally analyzed. "You don't suppose," he said, "that Penfield allowed the paper to be published on my word alone. He was much too careful to do that. He personally tested the sample for sulfite by smelling the evolved  $\text{SO}_2$  and by checking its decolorizing action on iodine solution. Then the paper was written and Penfield followed his usual custom of setting it aside for six months, after which he reread it, again tested for sulfite, and only then submitted it for publication." There the question must rest.

More important than his description of new minerals was Penfield's work in analyzing minerals whose composition had not been understood.

He established the correct formulas for amblygonite, argyrodite, auralchalcite, childrenite, the chondrodite group, cookeite, ganomalite, hanksite, herderite, howlite, ralstonite, staurolite, sulphohalite, topaz, and turquois. His work on the chondrodite group is a classic. By careful analyses Penfield determined the correct formulas for chondrodite, humite, and clinohumite, showed that they formed a morphotropic series, and predicted the probable existence of another mineral in the series. He wrote, "Thus  $\text{Mg}[\text{Mg}(\text{F}, \text{OH})]_2\text{SiO}_4$  is a possible and most likely compound to occur. This should crystallize either orthorhombic or monoclinic with  $\beta = 90^\circ$  and should have the axial ratio  $a:b:c = 1.086:1:1.887$ ." The mineral norbergite, with the predicted composition, was found 32 years later and the  $x$ -ray study by Taylor and West, with axes transformed to Penfield's position, gave the axial ratio  $a:b:c = 1.085:1:1.855$ .

He was much concerned about the role of water in minerals and successfully elucidated the composition of such minerals as topaz, herderite, and the chondrodite group on the basis of the isomorphism of hydroxyl and fluorine. In 1884, he pointed out that alkalis and water are present in beryl, and in 1890, that water is present in anthophyllite ("that the  $\text{H}_2\text{O}$  is an essential constituent of the mineral and is not the result of alteration is proved by the fact that it is very firmly united to the molecule, requiring an intense heat to drive it off . . ."). In 1907, Penfield and Stanley concluded, "That fluorine and hydroxyl present are integral parts of the amphibole molecule and that they are to be regarded as isomorphous with the protoxides is considered as definitely proven by the results of the analyses."

Penfield was not successful in elucidating the composition of the amphiboles or of tourmaline; these problems required the advent of  $x$ -ray structure determinations for their solution. But he was on the right track to present-day concepts of silicate frameworks with his postulate of a "mass effect," with "uniformity in structure of the acid part of the molecule."

Penfield's interests were by no means confined to the chemical aspects of mineralogy. He was an accomplished crystallographer and established the crystallography of many minerals and of a very large number of inorganic salts. He published several papers on the use of the stereographic and gnomonic projections. In his later years, he was much interested in the optical properties of minerals. In those days, before the advent of the immersion method, the determination of optical properties was not a simple matter. As G. T. Faust recently pointed out, Penfield was the first to show, in 1894, 1895, and 1896, how isomorphous substitution of OH for F, Mn for Fe, and Fe for Mg changed optical properties in isomorphous series. His versatility is well illustrated by his paper of 1890,

in which he described the new mineral spangolite,  $\text{Cu}_6\text{Al}(\text{SO}_4)(\text{OH})_{12}\text{Cl}\cdot 3\text{H}_2\text{O}$ , giving a chemical analysis in duplicate, blowpipe tests, the crystallography, results of etch tests, the optical properties, measurements of the hardness on different faces, and the specific gravity (determined in triplicate).

Penfield's personal qualities must have been as remarkable as his scientific achievements. The memorials cited below all are written in glowing terms of a kindly, patient teacher. I had the good fortune to be closely associated with three of his students, H. W. Foote, W. E. Ford, and C. H. Warren. All liked to talk about him, and 25 years or more after his death, his memory was dear to them all.

The portrait reproduced was made about 1902.

Memorials to Penfield were published by L. V. Pirsson, *Am. J. Sci.*, **22**, 353-367 (1906); J. P. Iddings, *Bull. Geol. Soc. Am.*, **18**, 572-582 (1902); H. L. Wells, *Nat. Acad. Sci., Biographical Mem.* **6**, 120-146 (1909), and H. A. Miers, *Mineralog. Mag.*, **14**, 264-268 (1907). Pirsson and Wells give complete bibliographies of about 100 papers; some of those referred to here are given below. All are from the *American Journal of Science*.

- (1884) On the occurrence of alkalis in beryl, **28**, 25-32.
- (1886) (with D. N. Harper). Chemical composition of herderite and beryl, **32**, 107-117.
- (1890) On spangolite, a new copper mineral, **39**, 370-378.
- (1894) (with W. T. H. Howe). Chemical composition of chondrodite, humite, and clinohumite, **47**, 188-206.
- (1894) (with J. C. Minor). Chemical composition and related physical properties of topaz, **47**, 387-396.
- (1895) (with J. H. Pratt). Effect of the mutual replacement of manganese and iron on the optical properties of lithiophilite and triphylite, **50**, 387-390.
- (1896) (with E. H. Forbes). Fayalite from Rockport, Mass., and the optical properties of the chrysolite group (4), **1**, 129-135.
- (1897) (with H. W. Foote). On roebbingite, a new silicate from Franklin Furnace, N. J., containing  $\text{SO}_2$  and lead, **3**, 413-415.
- (1901) The stereographic projection and its possibilities from a graphical standpoint, **10**, 1-24.
- (1907) (with F. C. Stanley). On the chemical composition of amphibole, **23**, 231-251.



PARAGONITE IN THE SCHIST OF GLEBE MOUNTAIN,  
SOUTHERN VERMONTJOHN L. ROSENFELD, *Wesleyan University, Middletown, Conn.*

During the writer's investigation of the metamorphic rocks of the Saxtons River area\* in southern Vermont, certain facts aroused curiosity concerning the composition of sericite in the chlorite-sericite schist on Glebe Mountain, one of the larger mountains comprising the eastern range of the Green Mountains. First of all the sericite is greasy-feeling. Secondly it occurs in a schist that is believed to be stratigraphically equivalent to the schist containing kyanite at Gassetts, Vermont (Thompson, 1950; Currier, 1934, p. 335-339). With this information in mind, J. B. Thompson suggested to the writer that the greasy-feeling mineral might well be pyrophyllite, the dioctahedral analogue of talc and also a mineral which had been described elsewhere in the region (Hitchcock et al., 1861, p. 504-505). Pyrophyllite would be expected to metamorphose to the higher grade assemblage, kyanite-quartz, found at Gassetts.

Accordingly a specimen of schist was collected at an elevation of approximately 2,215 feet above sea level on the west side of Glebe Mountain about 9,000 feet northeast of Winhall Station in the town of Londonderry. The schist at that locality consists of approximately 50% sericite (unspecified white mica(s)), 22% quartz, 18% chlorite, 5% magnetite, 2% epidote, 2% ilmenite, 1% garnet, and minor amounts of sphene, apatite, tourmaline, and albite. It was noted in immersion that the sericite consists of 2 micas. About 70% of the sericite consists of a very fine-grained approximately uniaxial mica. The remaining 30% is relatively coarser in grain size and has an optic angle more nearly characteristic of common muscovite ( $2V=40^\circ$ ).

The schist was crushed, and the fraction that passed through a 70 mesh screen and caught on a 200 mesh screen was saved for separation of the sericite. Separation was performed using a twofold method. Most of the magnetite, chlorite, ilmenite, epidote, garnet and tourmaline was removed magnetically. The sericite was separated from the remaining quartz, apatite, sphene, and albite by using a 500 cc. Pyrex beaker. It was noted that, when the relatively non-magnetic fraction was tumbled in the dry beaker, the sericite tended to cling preferentially to the wall

\* The material contained in this paper has been taken in large part from a dissertation, entitled, "*Geology of the southern part of the Chester dome, Vermont*," submitted in May, 1954, to the faculty of Harvard University in partial fulfillment of requirements for the degree of Doctor of Philosophy.



of the beaker. It proved a simple matter to pour off the predominantly granular fraction, recovering the sericite on a separate sheet of paper by giving the beaker a rather sharp blow. After considerable recycling to improve the purity of the sericite sample, about 3 grams were obtained and submitted to Forrest Gonyer for chemical analysis (Table 1). The

TABLE 1. CHEMICAL ANALYSIS OF SERICITE FROM SCHIST ON GLEBE MOUNTAIN, VERMONT  
(Spec. No. K34-1; Lab. No. 505, Department of Mineralogy, Harvard University)  
Analyst: Forrest Gonyer (May 11, 1949)

Weight %		Structure Formula*	
SiO <sub>2</sub>	44.41	K	0.19
TiO <sub>2</sub>	0.22	Ca	0.05
Al <sub>2</sub> O <sub>3</sub>	40.09	Na	0.76
Fe <sub>2</sub> O <sub>3</sub>	1.72	(Fe''	0.02)
FeO	0.28	(Mg	0.02)
MnO	0.02	Fe'''	0.11
MgO	0.16	(Ti	0.01)
CaO	0.67	Al	1.92
Na <sub>2</sub> O	5.80	Al	1.13
K <sub>2</sub> O	2.22	Si	2.87
H <sub>2</sub> O—	—	O	10.06
H <sub>2</sub> O+	4.45	(OH)	1.92
F	0.08	F	0.02
	100.12		
Less O = F	.03		
	100.09		

\* Elements included in parenthesis probably due to minor impurities.

structural formula calculated under the assumption that  $(O + (OH) + F) = 12$  appears alongside the chemical analysis. The calculated structural formula gives some indication of the purity of the sample and the accuracy of the analysis, as such a result could hardly be fortuitous. The small amounts of MgO, FeO, and TiO<sub>2</sub> in the analysis are probably due to minor amounts of chlorite and ilmenite that remained in the sample. It is clear from the analysis that the sericite consists largely of paragonite with subordinate muscovite either as a separate phase or in solid solution. The analysis further indicates a small amount of margarite, probably in solid solution.

X-ray powder diffraction photographs were taken of the sample using

a Straumanis-type Phillips camera with Fe-radiation and a Mn-filter. The diffraction lines are similar in relative arrangement and intensity to those of muscovite, although they differ in the values for  $\theta$ . The value of  $d_{(002)}$  based on the (006) and (0010) lines is  $9.60 \pm 0.02$  Å. This low value reflects the relatively small size of the sodium ions, which occupy the alkali positions in paragonite. There was no indication of separate resolution of muscovite lines in the observed photographs. This was undoubtedly the result of the low percentage of muscovite in the sample and the relative insensitivity of the film to reflections from minerals in low concentration.

At the writer's request in 1950 W. F. Bradley confirmed, using more sensitive x-ray equipment, the presence of two micas in the sample. Quoting with his permission, "The predominant phase is a mica of  $c \sin \beta$  length =  $9.65 (\pm .05)$   $\mu$  Å. It appears to be a two layer polytype analogous with muscovite; i.e.,  $c \sin \beta = 19.3$  Å. The secondary phase in abundance is of the order of 10%, and it is probably muscovite." Recently Evan Zen has resolved (006) and (0010) lines for both paragonite and muscovite in a similar schist of the same formation a few miles away. Both have confirmed the writer's earlier observation, based on studies in immersion, that the coarser mica is muscovite.

Optical methods do not at present appear very satisfactory for distinguishing between paragonite and muscovite generally. Schaller (verbal communication) has pointed out to the writer that many chemically normal muscovites have abnormally small optic angles similar to that here attributed to paragonite ( $2V \sim 0$ ). The indices of refraction for the coexisting micas in the Glebe Mountain sericite are remarkably close together. For the paragonite  $\beta \sim \gamma = 1.609$  using  $\text{Na}_D$  light. For the muscovite  $\gamma = 1.606$  and  $\beta = 1.604$ , and  $2V = 40^\circ$ . Due to distortion of the grains it was not possible to determine  $\alpha$  on either mineral accurately.  $\alpha \sim 1.580$  for both the paragonite and muscovite.

Further studies within the Saxtons River area show that the assemblage, paragonite-quartz, decomposes somewhere within the staurolite-kyanite zone, forming kyanite and sodic plagioclase. Also within the same zone, the assemblage, paragonite-ilmenite-quartz, decomposes into the assemblage, sodic plagioclase-staurolite-rutile. Such reactions point toward the deduction that paragonite is stable within the area only in the relatively lower grades of metamorphism (from the lower grade part of the staurolite-kyanite zone down). In the presence of calcite and quartz the paragonitic component of sericite breaks down within the garnet zone to give the assemblage, sodic plagioclase-zoisite. The parallel reaction of the assemblage muscovite-calcite-quartz to form the assemblage, microcline-zoisite, occurs in the higher grade part of the staurolite-

kyanite zone. The upper limit on the stability of paragonite is determined by its decomposition into sodic plagioclase and corundum. This latter assemblage was not observed in the Saxtons River area, probably because of the presence of quartz in most specimens examined.

As to the relatively finer grain size of paragonite relative to coexisting muscovite, it is of interest to note the parallel contrast in grain size between the sodic feldspar, albite, and the coexisting potassium feldspar, microcline (e.g. augen gneiss), in many metamorphic rocks. In both cases the sodic mineral tends to be finer grained than the potassic mineral.

Paragonite was found in one other type of occurrence within the Saxtons River area. The coarse micaceous alteration of kyanite in a boulder of kyanite-quartz rock found north of Houghtonville, Vermont (Town of Grafton), proved to be paragonite. The x-ray powder diffraction photograph (Fe radiation, Mn filter) was identical to that obtained for the sericite on Glebe Mountain. In addition  $\gamma \sim \beta = 1.610$ , similar to the indices of the paragonite from the schist within the limits of error. The optic angle of the mica from the pegmatite boulder is approximately  $5^\circ$ . Spectrographic analysis by Harrison showed Na greatly in excess of K in this mica.

In addition to those mentioned above, acknowledgment is due to Professor Esper S. Larsen, Jr., who guided the petrographic work entailed in the preparation of this paper. Thanks are due the Department of Mineralogy and Petrography at Harvard University for defraying the cost of the chemical analysis. Dr. Schaller made available to the writer his considerable knowledge concerning the paragonite problem. Harold Harrison performed a preliminary spectrographic analysis on the sericite, which was used to guide the chemical analysis. M. P. Nackowski has read the manuscript critically and has offered helpful comments.

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## ANTIGORITE: SUPERLATTICE AND STRUCTURAL FORMULA

J. ZUSSMAN, *University of Manchester, Manchester, 13 England.*

It is the purpose of this note to comment on two topics occurring in *The American Mineralogist*, Vol. 39, Nos. 9 and 10, 1954. First, the discussion by Brindley and von Knorring (1954) of the possible nature of the superlattice in antigorites from Unst, (Shetlands) and from Mikonui (New Zealand.) Secondly, the derivation of structural formulae for antigorites from chemical analyses, a matter which was dealt with by the above authors and also by McConnell (1954) in a note on "Ortho-antigorite and the tetrahedral configuration of hydroxyl ions." A similar topic was the subject of a note by Brindley (1954) concerning an antigorite from Caracas, Venezuela. (The localities Unst, Mikonui and Caracas will be denoted *U*, *M*, and *C* respectively in the following paragraphs.)

## THE SUPERLATTICE

On the powder photographs of antigorite (*U*) examined by Brindley, in addition to lines corresponding to an orthorhombic cell  $a=5.322$ ,  $b=9.219$ ,  $c=14.53$  Å, some were noted which were consistent with a super-lattice parameter  $S=43.8$  Å similar to that which occurs for antigorite (*M*) where  $S=43.5$  Å. In the latter instance Onsager (1952) had suggested that the superlattice resulted from an undulating sheet structure containing  $8\frac{1}{2}$  sub-cells in each large repeat distance in the "*a*" axis direction. This is one possible explanation in the case of antigorite (*U*) which Brindley rejects since  $8\frac{1}{2}$  times the sub-cell dimension is considerably greater than  $43.8$  Å ( $8\frac{1}{2} \times 5.322$  Å =  $45.24$  Å). It is here suggested that this fact does not rule out the undulating sheet possibility, for such a structure possessing  $8\frac{1}{2}$  repeats of the small cell along its curved surfaces would in fact result in a smaller repeat distance measured along straight lines parallel to the true cell axis. This concept fits well with the single crystal data obtained for antigorite (*M*) by Aruja (1945).

There is the important difference between the two cases however, that in antigorite (*M*) reflections cannot be indexed using a cell dimension  $a=5.32$  Å. If along reciprocal lattice row  $a^*$ , the 17th order reflection for the superlattice is taken as 2nd order of a sub-cell, then the latter has dimension  $a=5.12$  Å. If the 16th order is taken then the sub-cell has  $a=5.44$  Å. This is to be expected if the simple cell with  $a=5.32$  Å (i.e.,  $b/\sqrt{3}$ ) repeats only along a curve and not strictly in the true cell edge direction. Since the index *H* of strong superlattice reflections is sometimes a multiple of 16 and sometimes of 17 or of other integers, the value  $a=5.42$  KX, for antigorite (*M*) quoted by Brindley from Aruja's work has no special significance as a sub-cell parameter.

In the case of antigorite (*U*) reflections did occur precisely at points of a reciprocal lattice corresponding to  $a = 5.32 \text{ \AA}$  although at the same time other reflections were indexed for a super-cell with  $S = 43.8 \text{ \AA}$ . Assuming that the superlattice is related to the "*a*" parameter and not to "*c*" [it certainly is so in antigorite (*M*)], then since reflections of the sub-cell can only occur at large cell reciprocal lattice points, this implies that the true value of  $S$  is  $4 \times 43.8 \text{ \AA}$  (approx.  $33 \times 5.32 \text{ \AA}$ ). If this is so then there is no indication of sheet curvature, since  $5.32 \text{ \AA}$  is the normal repeat distance and occurs strictly along a straight line. It also means that for some reason reflections were observed only where  $H$  (the superlattice index) is a multiple of 4.

An alternative explanation of the Unst powder photograph is that it is in fact a superposition of two, one from a small cell serpentine mineral with  $a = 5.322 \text{ \AA}$  and a second from a large cell variety similar to antigorite (*M*); i.e. that two differently crystallized serpentine minerals are present in the specimen. A varying proportion of large cell variety may account for the different relative intensities of superlattice and normal lattice lines in photographs from different specimens.

#### *The Antigorite Formula*

The analysis by von Knorring of antigorite (*U*) No. 2 gave a structural formula, derived on the basis of  $9(\text{O}, \text{OH})$ , which did not accord very well with the ideal serpentine composition  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . A closer approximation to this composition was obtained on the basis of 2 Si atoms and by assuming the presence of approximately 10% of brucite impurity. An alternative interpretation of the chemical data was suggested by McConnell which involves the assumption that all the water including  $(\text{H}_2\text{O})-$ , which formed 1.26% of the sample, was essential to the crystal structure. Neither of these two assumptions would appear to be justified by experimental evidence and it is shown here that a reasonable interpretation of the analysis may be made without them.

In his note McConnell describes the use of von Knorring's analysis of antigorite (*U*) No. 2 to provide "further indirect evidence of the occurrence of hydrogens in substitution for silicon (i.e. tetrahedral hydroxyls)." The writer feels that since no agreed structural model has yet been adopted for ortho-antigorite the case chosen is not particularly suitable for this purpose. In the absence of data such as the measured density and the number of formula units per cell, in addition to the measured cell volume, a chemical analysis can give only atomic proportions. These may be used according to a structural concept to give numbers of atoms occupying the different atomic sites, and even this may be done in many different ways. As an example there is the case of antigorite



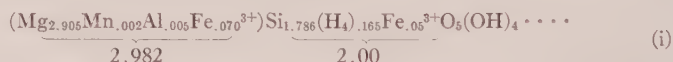
(C) for which Hess, Smith and Dengo (1952) derived two possible formulae, Brindley (1954) obtained a third, and a fourth based on a modified crystal structure was suggested by Zussman (1954).

A feature of several chemical analyses of antigorite has been that the ratio of octahedral to tetrahedral ions is less than that of the ideal formula, 1.5:1.0. This occurs again in antigorite (*U*) No. 1 described by Brindley and von Knorring, and may well be a necessary consequence of the crystal structure of certain antigorites. If therefore, a redistribution of ions similar to that suggested by McConnell results in a ratio nearer to 1.5:1.0 this need not be taken as evidence in favor of the new arrangement.

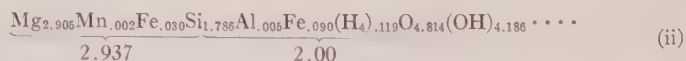
Even if this ratio is deemed desirable there is no need to make the assumption that  $(\text{H}_2\text{O})^-$  is structural water in order to achieve it. For the numbers of ions obtained by von Knorring are:



and using McConnell's suggestion of tetrahedral hydroxyls the various ions may be grouped in the following manner:

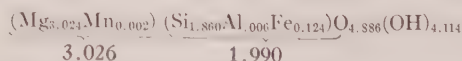


One should also consider the possibility that extra hydrogen atoms may occur in the structure as  $(\text{OH})^-$  replacing  $\text{O}^{2-}$ . This alternative and the dual role of trivalent ions in octahedral and tetrahedral positions, makes it possible to derive many different formulae from one set of atomic proportions. As a further example, if some of the extrahydrogens in antigorite No. 2 occur in hydroxyl ions replacing  $\text{O}^{2-}$  and some as  $4(\text{OH})^-$  in otherwise empty tetrahedral sites, the following formula may be obtained:



This is "designed" to be very similar to that given for antigorite (*U*) No. 1. It should be noted that formulae (i) and (ii) are obtained from the analysis without treating  $(\text{H}_2\text{O})^-$  as structural water, and without the assumption of brucite impurity.

By making a different and hardly less justifiable assumption, i.e. that 2.3% of the 15.03%  $(\text{H}_2\text{O})^+$  should be regarded as impurity, and calculating on the basis of 9 anions the following formula may be obtained:



This contains an appreciable amount of trivalent iron in tetrahedral positions, more than there is in antigorite (*U*) No. 1, but very little extra

hydrogen to be allocated an unusual role in the structure.

These examples illustrate that unless the weight of the unit cell content is known there is scope for a variety of interpretations of a chemical analysis taken as it stands, and still further variety if changes are made which have no strong experimental justification.

Finally I should like to point out that the method of calculation adopted by McConnell in his Table 1 (1954) has no essential new feature. McConnell's treatment differs from von Knorring's only in the assumption about  $(\text{H}_2\text{O})$ —. If this is excluded and the number of cationic charges is made 18 following the scheme of Table 1 pg. 830, the last column gives exactly the numbers of cations first obtained by von Knorring. This must be so since any formula based on an analysis expressed in terms of neutral oxides must itself be charge balanced. Therefore the assumption of 18 cationic charges per cell is equivalent to the assumption of 18 negative charges, i.e. 9 oxygen ions in the present case.

I am grateful to Dr. G. W. Brindley for providing opportunity to discuss some of the  $x$ -ray results prior to their publication.

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#### COMMENT ON DR. J. ZUSSMAN'S NOTE

Dr. Zussman has kindly allowed me to see the text of his note prior to publication. I agree with many of his points. There is undoubtedly a difficulty in understanding the superlattice parameter  $S=43.8$  and a normal pattern which indexes very well with  $a=b/\sqrt{3}=5.32 \text{ \AA}$ . The possibility that the material examined by  $x$ -rays may contain two kinds of structure was not seriously considered by the writer, although it was noted that the intensity of the entire group of superlattice lines varied from one sample of antigorite to another. It may be significant that the specimen showing the superlattice lines most clearly also showed in thin section the wavy thread-like bands which are illustrated in figure 1, plate 1, of the original paper (*Am. Mineral.*, **39**, p. 796, 1954). Dr. Zuss-

man's comments on structural formulae are apposite. Von Knorring and I assumed a brucite impurity but admitted the slender nature of the evidence, McConnell invoked tetrahedral hydroxyl groups and Zussman now shows this concept can be variously applied; he also considers "a different and hardly less justifiable assumption" that 2.3% of the 15.03% of  $\text{H}_2\text{O}+$  should be treated as an impurity. This later suggestion appears to be just about as arbitrary as our brucite suggestion and it is scarcely strengthened by the Fe atoms going wholly into tetrahedral positions. What emerges most clearly from these discussions is that structural formulae are difficult to determine reliably when departures from normality arise. Under such circumstances, it is obviously desirable to survey the problem from a variety of points of view before attaching much weight to an unusual formula arrived at from one set of assumptions.

G. W. BRINDLEY

#### NOVACEKITE FROM THE WICHITA MOUNTAINS, OKLAHOMA

W. T. HUANG,\* *Syracuse University, Syracuse, N. Y.*

Novacekite,  $\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ , described by Frondel (1951) from Schneeberg, Saxony, has been identified from the Wichita Mountains in Southwest Oklahoma. This member of the torbernite group was first found in October 1952 by Earl Smith, in Permian Red Beds and recent sedimentary deposits in SE  $\frac{1}{4}$ , SE  $\frac{1}{4}$  Sec. 23, T. 3 N., R. 14 W., when the writer accompanied him in selecting a problem for his Master's thesis in the Wichita Mountains. Later, in April 1953 novacekite was again found in a friable red sandstone,  $\frac{1}{2}$  mile northwest of Twin Mountain, while the writer undertook the investigation of the Wichita Mountains igneous complex. Small cavities of the sandstone are filled with novacekite crystals along with limonite, malachite, calcite and quartz grains. The occurrences of novacekite in sandstone are reminiscent of that recently described by Stern and Ansell (1954). They found the same mineral from the Woodrow area, Laguna Reservation, Valencia County, New Mexico. The novacekite coats a somewhat iron-stained friable sandstone in the Westwater Canyon sandstone member of the Morrison formation of Jurassic age.

Novacekite forms a series with saléeite,  $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ , its phosphate analogue. Frondel divides this phosphate-arsenate series and applies the species names saléeite and novacekite to the halves of the series with  $\text{P} > \text{As}$  and  $\text{As} > \text{P}$ , respectively, in atomic per cent. The speci-

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men collected by Smith is somewhat altered and is coated with impurities. The amount of material present in the specimen found by the writer was insufficient for a quantitative chemical analysis. However, a semi-quantitative spectrographic analysis of the Oklahoma novacekite indicated  $\text{As}_2\text{O}_5$  in the greater-than-10 per cent bracket, but  $\text{P}_2\text{O}_5$  was not observed in any bracket down to a sensitivity limit to 0.1 per cent.

The novacekite is straw yellow in color. Euhedral crystals are rectangular in shape. The basal cleavage is perfect and luster is waxy. The specific gravity is 3.66.

X-ray studies showed this novacekite to be tetragonal. The unit cell dimensions are:  $a_0 = 7.18 \text{ \AA}$ ,  $c_0 = 20.16 \text{ \AA}$ . Thus, the x-ray powder pattern of novacekite differs from the patterns of saléeite and arsenatian saléeite only by its slightly larger unit cell dimensions. (The unit cell dimensions of arsenatian saléeite are:  $a_0 = 7.05 \text{ \AA}$ ,  $c_0 = 19.87 \text{ \AA}$ .)

Optically this mineral is anomalously biaxial with  $(- )2V_D = 5^\circ - 18^\circ$ . Indices of refraction for  $D$  light at  $25^\circ \text{ C}$ . are:  $\alpha = 1.624$ ,  $\beta = \gamma = 1.640$ . Pleochroism is weak:  $X$  = nearly colorless,  $Y = Z$  = yellow to pale yellow. The mineral fluoresces bright straw yellow to lemon yellow in both short and long wave-length ultraviolet radiation, though the intensity of the fluorescence is somewhat less in short wave-length than in long wave-length radiation.

The writer wishes to express this appreciation to Mr. Earl Smith, graduate student of the University of Oklahoma, for the specimen that he contributed to this investigation, and to Professor Earl T. Apfel, Director of Geo-Research at Syracuse University Research Institute, who kindly read the manuscript.

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#### AN UNUSUAL PALAGONITE TUFF

DUNCAN McCONNELL, *College of Engineering, The Ohio State University, Columbus, Ohio.*

About a decade ago a fine-grained, black rock specimen was submitted to the laboratories of the Bureau of Reclamation, U. S. Department of the Interior, Denver, Colorado. The hand specimen had a satin-like luster and conchoidal fracture, giving it the appearance of cannel coal. It came from a complex series of flows and beds of volcanic origin,  $6\frac{1}{2}$  miles east of Vantage, Washington. According to Dr. William H. Irwin, who later



visited the locality and collected further samples, the rocks of the vicinity show great diversity in color, texture, and structure, and show evidences of significant alteration. He further commented that it is not necessarily possible from examination of a hand specimen to ascertain which rocks are lavas and which are altered tuffs.

Microscopically, the rock is observed to consist of many small bodies of a dark greenish-brown substance contained within a colorless matrix (Fig. 1). This dark-colored substance shows weak anisotropism and a moderate range in refractive index. In general the refractive index is slightly below 1.495, but measurements as high as 1.510 were obtained.

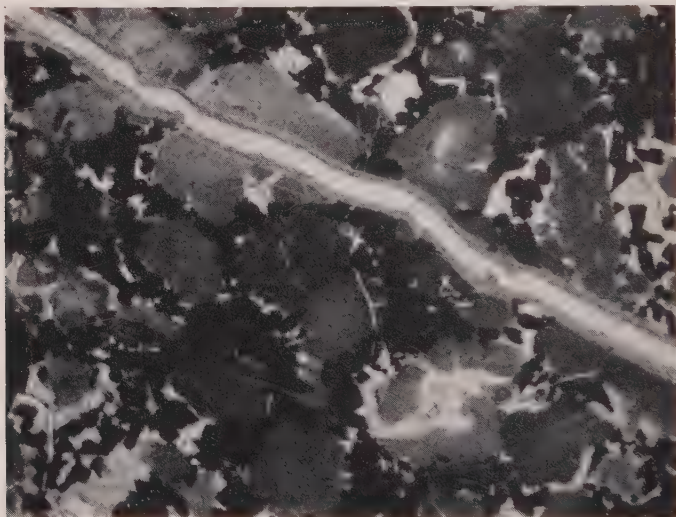


FIG. 1. Representative area of palagonitic bodies, magnetite crystals and opaline matrix of specimen which is virtually devoid of carbonation. The chalcedonic veinlet has opaline margins. Magnification 117 $\times$ ; without analyzer.

The term, palagonite, has been applied to such dark-colored, altered, glassy materials. Its use is retained with the reservation that it does not denote a mineral species. About half of the volume of the rock is composed of these bodies of palagonite; they average 0.15 mm. and are fairly uniform in color and shape.

The colorless matrix is opal with a refractive index ranging from 1.455 to 1.435. The opal also shows weak anisotropism and appears to be microcrystalline in certain portions. Although these phenomena suggest the presence of tridymite or cristobalite, material with appropriate refractive indices for these minerals was not isolated. Chalcedonic varieties of silica occur as irregular bodies and veins (Fig. 1).



The third essential constituent of the rock is fine, granular magnetite. Carbonates occur in variable amounts within and substituting for the opaline matrix, sometimes almost to the exclusion of the latter (Fig. 2). A few small, detrital grains of quartz, feldspar, and mica were observed. Although zeolites were not detected in the thin sections examined, their complete absence would be unlikely in a rock of this type.

Occasional particles of a diabasic rock were observed in the thin sections, one of which was as large as 6 mm. (Fig. 2). This rock fragment has been highly altered so that the relict feldspar laths now are composed essentially of carbonates.

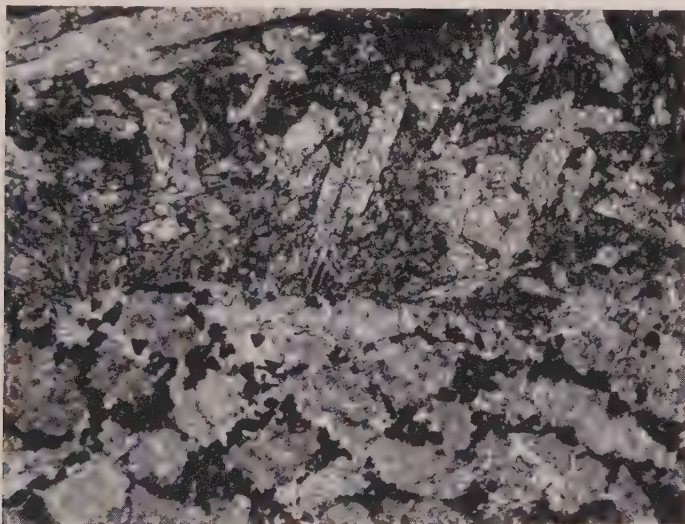


FIG. 2. Specimen showing intensive carbonation. The upper half is a fragment of diabase showing relict feldspar laths. Magnification 85 $\times$ ; without analyzer.

The water content of this rock is considerably below the range, 14.2 to 24.4 per cent, reported by Tyrrell and Peacock (1926) as is indicated by an ignition loss of only 9.1 per cent. However, alteration of the state of oxidation of the iron compounds could contribute to an error in the direction of a low result. More important is the fact that a significant volume of the rock is magnetite which has a high specific gravity but contributes no water. The ignition loss was determined on a sample containing little, if any, calcite.

In attempting to reconstruct the geologic history of the rock several factors must be considered. The palimpsest textures of the rock particles imply a basaltic composition, but the types of alteration observed do not necessarily imply that these lithic fragments were subjected in situ to the

same alteration processes as the main material of the rock. The uniform textural characteristics of the bulk of the rock show no relationship to any primary igneous texture. In view of the predominance of palagonitic bodies, it is presumed that the rock was originally deposited as a vitric tuff of basaltic composition, which subsequently has been highly altered through silicification and carbonation. The highest temperature phase of the metasomatic processes presumably produced recrystallization of or introduction of iron-bearing substances to yield magnetite. In view of their very small size and their usual occurrence interstitially among the palagonitic bodies, it is unlikely that the magnetite crystals existed in their present form in the unaltered tuff.

Although palagonite tuffs probably are not items of great rarity, and may be fairly common in certain localities, the rock described here presents several interesting features. The most unusual characteristic is the uniformity and peculiarity of its texture.

The writer is indebted to his former colleagues with the Bureau of Reclamation. William H. Irwin supplied information on the field occurrence and William Y. Holland made the photomicrographs. L. N. McClellan, Assistant Commissioner and Chief Engineer, granted permission to publish this information.

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#### NEW OCCURRENCES OF NATIVE SELENIUM

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Native selenium has been identified in three localities during the course of study of the mineralogy of uranium in sandstone-type deposits, conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

In June 1953 William Braddock collected several pieces of friable sandstone from the Road Hog No. 1A mine in the southern part of the Black Hills, Fall River County, S. Dak. Uranium and vanadium ores are being mined there in the Lakota sandstone of Early Cretaceous age. The sandstone contained small purple-gray metallic acicular crystals as felty aggregates on fracture surfaces and disseminated throughout the sandstone. The crystals were later identified as native selenium on the basis of x-ray studies by M. E. Thompson and qualitative chemical analysis by F. S. Grimaldi of the Geological Survey.

In the spring of 1954, Carl Roach collected samples of high-grade vanadium-uranium ore from the Peanut mine, Bull Canyon, Montrose County, Colo. The Peanut mine is in the Salt Wash sandstone member of the Morrison formation of Late Jurassic age. The ore samples contained two new quadrivalent vanadium minerals and abundant crystals of native selenium.

A sample collected in June 1954 by M. E. Thompson from the Parco No. 23 mine, Thompsons district, Grand County, Utah, contained crystals of native selenium associated with zippeite, metatyuyamunite, metarossite, montroseite, and corvusite. The Parco No. 23 mine is also in the Salt Wash sandstone member of the Morrison formation.

The physical properties of the selenium from the three localities are similar. It occurs as purple-gray metallic acicular crystals, usually as felty aggregates of very small crystals. The largest of the crystals is not more than 2 mm. in length. By transmitted light the crystals are nearly opaque, but they transmit red light and show parallel extinction. By reflected light they are anisotropic and dichroic (creamy white and darker).

Native selenium was reported from several carnotite deposits of the Colorado Plateau by Hillebrand, Merwin, and Wright (1914) on the basis of sublimation tests. The selenium crystals described above give a red sublimate in the closed tube. Although selenium is not easily recognized in the hand specimen, further occurrences of native selenium will undoubtedly be found in sandstones containing uranium and vanadium minerals.

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#### AGE DETERMINATION OF ZIRCON CRYSTALS FROM CEYLON\*

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#### INTRODUCTION

Zircon crystals from Ceylon have long been known to gemmologists for their abundance and high quality as semiprecious stones. Because of extraordinary variations in physical properties, such as the indices of refraction and density, they have captured the attention of mineralogists for almost the last 100 years. However, very little is known regarding

\* Publication authorized by the Director, U. S. Geological Survey.

their age. Wadia and Fernando (1944) suggest a pre-Cambrian age for the pegmatites from which the zircon of the gem-bearing gravels is believed to have been derived.

#### ANALYTICAL PROCEDURES

In making age determinations on 21 crystals of gem quality zircons from Ceylon, the alpha-particle emission of each sample was measured by a thick-source alpha-counting method in an ionization chamber. The counting rates, corrected for absorption, geometry, and background counts, were converted to units of alpha per milligram per hour assuming a theoretical absorption factor of  $2.22 \times 10^{-3}$  for zircon. For each sample a sufficient number of counts were recorded to reduce the probable counting error to less than 2 per cent.

The lead content of each sample was determined quantitatively by a recently developed spectrographic method (Waring and Worthing, 1953). This method is applicable to samples containing as little as 1 ppm lead with an error of less than 10 per cent.

Fluorimetric uranium analyses were made on 12 of the zircon samples and are believed to be accurate to  $\pm 5$  per cent.

Equivalent uranium may be estimated from the alpha counts using the following equation:

$$eU \text{ (per cent)} = 2.75 \times 10^{-4} I$$

where  $I$  is the activity index in  $\alpha$ /mg./hr. The ratio  $U/eU$  (column 5, Table 1) ranges from 0.83 to 1.17. The average of the ratios, 1.01, indicates that the alpha activity is due principally to uranium. A small amount of thorium may be present in those samples where the  $U/eU$  ratio is considerably less than 1.00.

#### AGE CALCULATIONS

The ages were determined by a modification of the lead-alpha activity method described by Larsen and others (1952). The modifications used will be described more fully in another paper. The approximate age was first calculated for all the specimens from the formula

$$t = \frac{2600 \text{ Pb}}{\alpha} \quad (1)$$

where  $t$  is the age in millions of years, Pb is the lead content in parts per million, and  $\alpha$  is the alpha activity per milligram per hour. The constant, 2600, is based on the assumption that these zircon samples contain little or no thorium. As these ages are older than 300 million years, a correction was made similar to that described by Keevil (1939). Thus

$$t = t_1 - \frac{1}{2} k t_1^2 \quad (2)$$

TABLE 1. AGE OF ZIRCON FROM CEYLON

Sample	$\alpha$ /mg/hr	Lead (ppm) <sup>1</sup>	Uranium (ppm) <sup>2</sup>	$U/eU$	Age (M.Y.) <sup>3</sup>	Corrected age (M.Y.) <sup>4</sup>
1	103	22	330	1.17	526	554
4-33	150	37	410	0.99	602	603
2	273	65	730	0.97	583	580
3-16	352	80			558	
5-1	380	88			568	
4-36	430	91			521	
3-11	533	115			530	
3	643	150	1470	0.83	571	546
3-42	649	143			542	
2-37	652	148			556	
2-13	850	196			566	
4	882	205	2470	1.02	569	575
2-18	913	200	2300	0.92	539	527
2-23	985	227			565	
6	1185	275	3580	1.10	569	587
2-17	1245	270	3180	0.93	532	524
7	1583	392	4760	1.09	604	623
9	1815	450	4880	0.98	604	603
1-2	2040	440			530	
10	2197	529	6450	1.06	587	602
1-26	2210	498	6280	1.03	553	560
Average				1.01	561 $\pm$ 26	574 $\pm$ 32

<sup>1</sup> Determined spectrographically by C. L. Waring, U. S. Geological Survey.

<sup>2</sup> Determined fluorimetrically by F. Cuttitta, U. S. Geological Survey.

<sup>3</sup> Approximate age in millions of years, calculated from equations (1) and (2).

<sup>4</sup> Age in millions of years, corrected for possible thorium.

where  $t_1$  is the approximate value given by equation (1) and  $k$  was chosen as  $1.90 \times 10^{-4}$  for these specimens, the  $Th/U$  ratios being very close to zero.

As there may be a minute amount of thorium in some of these specimens, more accurate determinations were made on 12 of the samples. By making a uranium analysis thorium, if present, can be determined by difference to yield a more accurate value for the constant in equation (1) and for  $k$  in equation (2).

The ages based on equations (1) and (2) for all the zircon samples are shown in Table 1. The ages for 12 zircon samples on which uranium analyses have been made are shown in column 7.



## DISCUSSION

The possible loss of uranium, thorium, their radioactive daughter products, and lead by natural leaching or other geologic processes must be considered for the suite of samples. Several samples of varying lead and alpha-activity content have been acid treated in 1:1 aqua regia at a temperature of 80° C. for half an hour. Alpha activity and lead determinations on the acid-treated material showed no measurable change. It is therefore assumed that natural leaching has not altered the  $Pb/U$  ratio of the zircons. The good agreement of the ages over the range of samples tends to bear out this assumption. All the lead is believed to be of radiogenic origin. The presence of any original lead in the zircon structure, that is, lead present at time of crystallization of the zircon, should show up in a sample of very low lead content. For example, in sample 1 which contains 22 ppm of lead, the result would be an appreciably greater age than the average if significant amounts of original lead were present.

The average age of the suite of 21 zircon crystals as determined by the Larson method is 561 million years, and the age of the 12 samples corrected for possible thorium is 574 million years. The age of the gem-type Ceylon zircon is probably about 570 million years. A geologic time table compiled by Marble (1950) shows that this value is equivalent to late pre-Cambrian age.

Holmes (1927) obtained 585 million years from the average lead-uranium ratios in a thorianite from Ceylon. In his calculations he used the approximate formula for young rocks. Using the correction (equation 2), this age would now be calculated as approximately 565 million years.

Nier (1939) extracted the lead from a thorianite sample from Ceylon and analyzed it isotopically. The results of this analysis—531, 461, and 485 million years from the  $Pb^{206}/U^{238}$ ,  $Pb^{208}/Th^{232}$ , and  $Pb^{207}/Pb^{206}$  ratios, respectively. On a specimen of Ceylon zircon, Tilton and Aldrich (1955) have recently obtained 540, 544, 555, and 538 million years from the  $Pb^{206}/U^{238}$ ,  $Pb^{207}/U^{235}$ ,  $Pb^{207}/Pb^{206}$ , and  $Pb^{208}/Th^{232}$  ratios, respectively.

The authors are indebted to Professor Larsen for guidance and helpful suggestions and to Dr. H. Holland for supplying the samples and for his constructive criticism.

This work was done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

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#### VANNEVAR BUSH FELLOWSHIPS IN EARTH SCIENCES

A Joint Educational Program of Massachusetts Institute of Technology and  
Carnegie Institution of Washington

The Department of Geology and Geophysics of the Massachusetts Institute of Technology and the Geophysical Laboratory of the Carnegie Institution of Washington are cooperating in the award of pre-doctoral fellowships in theoretical and experimental geology. The awards are to be known as the Vannevar Bush Fellowships in Earth Sciences, in honor of Dr. Bush who long served as Professor, and later as Dean and Vice President, at M.I.T. and more recently as President of the Carnegie Institution of Washington. Candidates for an award must have advanced training in mathematics, physics and chemistry, and a broad knowledge of the earth sciences. Recipients will have unusually favorable opportunities to do thesis work on challenging new problems in the most active and rapidly moving fields of earth science.

Applicants for the award must have completed all M.I.T. requirements for the Ph.D. degree except thesis, and will be registered as full-time doctoral candidates at M.I.T. during that part of their graduate study in which they are in residence at the Geophysical Laboratory. The fellowship will be awarded for the period required by the recipient to complete his laboratory work at the Geophysical Laboratory, and the subsequent time required at M.I.T. for analyzing and correlating the data and completing the dissertation. In general, fellows should expect to spend at least three or four terms in Washington and one or two terms in Cambridge.

While at the Geophysical Laboratory, the Fellow will receive \$200 per month (plus appropriate tuition) for the first 12 months and \$225 per month (plus tuition) for the duration of the fellowship. Upon returning to M.I.T., the recipient will continue to receive the same monthly stipend as last received from the Geophysical Laboratory, in addition to tuition.

At all stages of his work, the Fellow will be registered at M.I.T. as a full-time doctoral candidate, and will work under the close supervision of at least one faculty member of the M.I.T. Department of Geology and Geophysics.

Any graduate student interested in preparing for competition for the awards should write to the Chairman, Department of Geology and Geophysics, 24-302 M.I.T., Cambridge 39, Massachusetts, for information about entrance requirements and possible financial assistance while meeting M.I.T. requirements.

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The Russian mineralogist Konstantin Konstantinovich, born March 5, 1875, died Dec. 21, 1954.

## BOOK REVIEWS

LEHRBUCH DER MINERALOGIE, by W. SCHMIDT AND E. BAIER. Second Edition, revised and enlarged by E. Baier, 376 pp., 302 illustrations and one colored plate, 16×24 cm. Birkhäuser Verlag, Basel, Switzerland, and Stuttgart, Germany, 1955. Price, bound, 35 DM.

The first edition of this text was published in 1935 and reviewed in considerable detail by J. W. Gruner (Vol. 21, p. 267). The senior author, Professor W. Schmidt, died April 25, 1945, and accordingly the text was revised by the junior author, E. Baier.

The method of presentation follows rather closely that of the first edition. Many of the chapters have been expanded, which is especially true of the one on geometrical crystallography. The descriptions of the minerals leave much to be desired. In fact, it is questionable whether students can obtain a satisfactory knowledge of the various properties which are important in the rapid recognition of many of the minerals described, and of their principal localities. A bibliography of 4½ pages has been added, and the book as a whole increased by 56 pages.

The text is well bound, but the price is relatively high.

EDWARD H. KRAUS,  
*University of Michigan,  
Ann Arbor, Michigan*

CLAYS AND CLAY MINERALS, EDITED BY ADA SWINEFORD AND NORMAN PLUMMER. National Academy of Sciences, *National Research Council Publ.* 327, viii+498+index. Washington, D. C., 1954 (1955), \$4.00. (Proc. 2nd Natl. Conference on Clays and Clay Minerals, Columbia, Mo., Oct. 15-17, 1953).

This volume is a "must" for all persons who would attempt to keep abreast of this rapidly expanding area of knowledge. As indicated in the introduction, the contributors are ceramists, chemists, crystallographers, geologists, mineralogists, petrographers, physicists, soil scientists, and several types of engineers, if any such simple classification is feasible.

The volume includes 36 scientific contributions on genesis and occurrence, methods of identification, fundamental studies in mineralogy or crystallography or chemistry, and miscellaneous topics. Much of this information has not been published elsewhere. A guide to the field trip is included.

Mineralogists should be more than casually interested in the discussion on pages 344-348, where a phase-rule chemist and a physicist (crystallographic) discuss "... a thorough overhaul of the nomenclature of the clay *minerals*..." (Italics mine). That such an "overhaul" is "long overdue" is probably true, but it is hoped that a mineralogist will be invited to attend this conference when it convenes, even if he merely acts as an observer.

The editors are to be complimented on the excellence of their work. The quality of the book meets the highest standards in all respects.

DUNCAN McCONNELL,  
*Ohio State University, Columbus, Ohio*

## NEW MINERAL NAMES

### Evenkite

In the abstract published in *The American Mineralogist*, **40**, 368 (1955), the composition of evenkite was given as  $C_{12}H_{42}$ . Mr. Arthur W. Rudkin, Earlwood, New South Wales, has kindly called attention to the fact that this formula does not agree with the analysis. Examination of the original paper shows that the formula was there given as  $C_{21}H_{42}$ . However, Mr. Rudkin also points out that one would expect a saturated hydrocarbon of formula  $C_nH_{2n+2}$ , and the analysis actually corresponds much more closely to  $C_{21}H_{44}$  than to  $C_{21}H_{42}$ . My apologies for the error and my thanks to Mr. Rudkin.

MICHAEL FLEJSCHER

### Labuntsovite

E. I. SEMENOV AND T. A. BUROVA, On the new mineral labuntsovite and on the so-called titanoeplidite. *Doklady Akad. Nauk. S.S.S.R.*, **101**, 1113–1116 (1955) (in Russian).

The name titanoeplidite was given by Labuntsov in 1926 (See *Am. Mineral.*, **12**, 295 (1927)) to a mineral from Khibina resembling elpidite in crystallography but shown qualitatively to contain much titanium. Re-examination of the original material and of samples found in the Lovozero massif show this to be a new mineral.

Orthorhombic, in simple prismatic crystals up to  $12 \times 3 \times 2$  mm., showing the forms  $c$  (001),  $b$  (010),  $m$  (110),  $d$  (011), and  $s$  (111).  $a:b:c = 0.511:1:0.489$  (elpidite has  $0.5117:1:0.9781$ ). X-ray powder data are given for both localities; the strongest lines (Lovozero) are 3.15 (10), 2.56 (9), 1.543 (9), 3.09 (8), 1.677 (8); the pattern for elpidite is different. Cleavage perfect on (100).

Color rose to brownish-yellow. Brittle. Hardness about 6.  $G = 2.901$  (Lovozero), 2.96 (Khibina). Optically biaxial, positive,  $ns \alpha = 1.689$ ,  $\beta = 1.702$ ,  $\gamma = 1.795$ ,  $2V \ 41^\circ$  (Lovozero)  $\alpha = 1.686$ ,  $\gamma = 1.792$  (Khibina). The optic axial plane is (001),  $X = b$ ,  $Y = c$ ,  $Z = a$ . Pleochroic from brownish-yellow on Z to yellowish on X.

Analysis by T.A.B. of rose-colored material from Lovozero gave  $SiO_2$  39.59,  $Al_2O_3$  1.30,  $Fe_2O_3$  1.56,  $Nb_2O_5$  1.45,  $TiO_2$  25.49,  $MgO$  0.42,  $MnO$  2.34,  $CaO$  1.19,  $BaO$  "6.61" (see note below),  $K_2O$  7.23,  $Na_2O$  3.18,  $H_2O$  7.91; sum "100.27%." (Note—this adds to 98.27. However, the atomic ratios given indicate that  $BaO$  should be 8.61%. M.F.). This corresponds to  $(K, Ba, Na, Ca, Mn)(Ti, Nb)(Si, Al)_2(O, OH)_{7.0}6H_2O$  (more nearly  $1 H_2O$ . M.F.). X-ray spectral analysis showed Rb (0.3%), Sr, Y, Ce, and Th, and spectrographic analysis by L. N. Indichenko showed also Be, Pb, Zn, Cu, Sn, and V (weak lines). The water is lost gradually between  $200^\circ$  and  $400^\circ$  C. (dehydration curve by O. V. Karpov given). The mineral dissolves with difficulty in  $HCl$ ,  $HNO_3$ , or  $H_2SO_4$ . Easily fusible before the blow-pipe to a bluish enamel.

Labuntsovite is widely distributed in the Lovozero and Khibina alkalic massifs, in druses with albite and natrolite, and associated with aegirine, nepheline, microcline, eudialyte, ramsayite, and murmanite. It is a hydrothermal alteration product of murmanite and is sometimes altered to anatase (leucoxene).

Since the mineral is not related to elpidite, the name titanoeplidite should be dropped. Labuntsovite is named for Aleksander Nikolaevich Labuntsov and Ekaterina Eutikhieva Labuntsov-Kostyleva, Russian mineralogists.

M. F.

### Ferutite

A note in Zapiski Vses. Mineral. Obshch. (*Mém. soc. russe minérale*), **83**, No. 4, p. 425 (1954) states that at the meeting held May 24–27, 1954, Yu. V. Kazitsyn gave a paper in



which he stated that *x*-ray study of the "mineral from Mozambique" showed it to be different from davidite. It is hexagonal with  $a\ 6.88kX$ ,  $c\ 16.86kX$ . It is given the name ferutite (from ferrum, uranium, titanium). Presumably this is the davidite-like mineral described by Bannister and Horne, *Mineral. Mag.*, **29**, 101–112 (1950), from the Tête district, who reported it to be hexagonal rhombohedral (class  $3m$ ), with  $a:c=1:1.37$ .

M. F.

### Mavudzite

A<sup>o</sup>. VASCONCELOS PINTO COELHO, O minério de urânio de Mavudzi—Tete (Moçambique). *Garcia de Orta (Rev. junta missões geogr. e invest. do Ultramar)* **2**, No. 2, 209–219 (1954). The name mavudzite is given to the radioactive mineral from Mavudzi, Tete district, Mozambique, described by Bannister and Horne, *Mineral. Mag.*, **29**, 101–112 (1950). Ten new partial analyses are given.

DISCUSSION: Bannister and Horne stated "It does not seem warrantable to claim that the radioactive mineral from Tete, Mozambique, is a new and distinct species. It should rather be classed as a variety of davidite until unambiguous evidence to the contrary is forthcoming." On this basis, the name mavudzite should not have been proposed.

M. F.

### Grovesite

F. A. BANNISTER, M. M. HEY, and W. CAMPBELL SMITH, Grovesite, the manganese-rich analogue of berthierine. *Mineral. Mag.*, **30**, 645–647 (1955).

A micro-analysis (on 70 mg. for main constituents, 60 mg. for  $H_2O$ , and 20 mg. for oxidation states) gave  $SiO_2\ 22.0$ ,  $Al_2O_3\ 18.8$ ,  $Fe_2O_3\ 4.1$ ,  $MnO\ 43.4$ ,  $MgO\ 0.8$ ,  $BaO\ 0.3$ ,  $H_2O\ 9.0$ ; sum 98.4%, corresponding to  $(Mn, Fe, Al)_{12} (Al, Si)_8 O_{22} (OH)_{14}$  or  $(Mn, Fe, Al)_3 (Al, Si)_2 (O, OH)_9$ . This is close to the composition of pennantite (see *Am. Mineral.*, **32**, 256 (1947)), but the *x*-ray powder data (not given) do not resemble closely those of chlorites. They agree well with those for cronstedtite and berthierine except that grovesite shows a fairly strong line corresponding to a spacing of  $14\ \text{\AA}$ . The mineral is therefore a member of the cronstedtite-berthierine-amesite group with a structure based on the two-layer sheets of the kaolin family, but presumably with a two-sheet repeat as compared with the three-sheet repeat of cronstedtite. Berthierine (not berthierite) (Beudant, 1832) was formerly thought to be identical with chamosite, but is structurally distinct. (The name berthierine ought to be changed to eliminate confusion. M.F.)

Grovesite is dark brown (blackish-brown). It occurs as small rosettes, at most 0.5 mm. across.  $D=3.150\pm.02$ . The unit cell dimensions are  $a\ 5.51\pm.02$ ,  $b\ 9.54\pm.02$ ,  $c\ 14.36\pm.04\ \text{\AA}$ . It is optically uniaxial, negative with  $n_s(Na)\alpha'=1.658\pm.001$ ,  $\beta=\gamma=1.667\pm.001$ , absorption  $\beta=\gamma>\alpha$ ;  $\beta$  and  $\gamma$ , parallel to the cleavage, very dark brown;  $\alpha$ , perpendicular to the cleavage, red-brown.

The mineral is from the No. 5 ore-body of the Benallt mine, Rhiw, North Wales. The name is for A. W. Groves, geologist, Colonial Geological Surveys.

M. F.

### Trogtalite, Hastite, Bornhardtite, Unnamed Cobalt Selenide

PAUL RAMDOHR AND MARG. SCHMITT, Vier neue natürliche Kobaltselenide von Steinbruch Trogtal bei Lautenthal im Harz. *Neues Jahrb. Mineral., Monatsh.* 1955, No. 6, 133–142.

Four new cobalt selenides occur in fine violet to red-brown intergrowths in clauthalite; hematite and native Se (secondary) are also present. Samples were drilled out under the microscope; the *x*-ray patterns were corrected for the presence of clauthalite.



*Trogtalite*. Isotropic, very hard, polishes badly, color rose-violet. The  $x$ -ray powder pattern was indexed as cubic with  $a_0$   $5.87 \pm 0.02$  Å. Synthetic  $\text{CoSe}_2$  (pyrite type) has  $a_0$  5.854 Å. The name is for the locality. It probably also occurs at St. Andreasberg, Harz.

*Hastite*. Strongly anisotropic, hard, polishes well. Forms idiomorphic and radiating crystals. Reflection pleochroism strong, especially in oil immersion, and corresponds to orthorhombic symmetry. Color light brownish-red to dark reddish-violet. Twinning observed. These properties suggested that the mineral might be  $\text{CoSe}_2$  of marcasite type or  $\text{CoAsSe}$  of arsenopyrite type, neither of which has been synthesized.  $X$ -ray powder data were indexed in terms of a cell  $a_0$  3.60,  $b_0$  4.84,  $c_0$  5.72 Å and comparison with marcasite,  $\text{FeSe}_2$ , and frobergite indicates this to be  $\text{CoSe}_2$  of marcasite type. The name is for Dr. P. F. Hast, mining engineer.

*Bornhardtite*. Rose-colored, but paler than the preceding two. Isotropic. Hardness about 4 or a little less. The  $x$ -ray powder diagram is indexed as cubic, with  $a_0 \sim 10.2 \pm 0.2$  Å, which indicates a mineral of the linneite group,  $\text{Co}_3\text{Se}_4$ . This may be closely related to the unnamed cobalt copper nickel selenide ( $\text{Co}:\text{Cu}:\text{Ni}=3:2:2.5$ ) from Goldfields district, Saskatchewan, which had  $a_0$  10.005 Å (Robinson and Brooker, *Am. Mineral.*, **37**, 542–544 (1952)). The name is for the late Dr. W. Bornhardt.

*Unnamed Mineral*. Anisotropic, softer and polishes better than trogtalite and hastite. Optical relations and hardness are analogous to those of niccolite, but the color is more of a violet-rose, not yellowish. The mineral was so scarce that  $x$ -ray powder diagrams were unsatisfactory. Weak lines that were measured gave a pattern of NiAs type corresponding to  $a_0$  3.6,  $c_0$  5.3 Å. Synthetic  $\text{CoSe}$  has  $a_0$  3.59,  $c_0$  5.27 Å. No name is proposed pending further study.

M. F.

### Nolanite

S. C. ROBINSON, Mineralogy of uranium deposits, Goldfields, Saskatchewan. *Canada Dept. Mines and Techn. Surveys, Geol. Survey Canada, Bull.* **31**, 128 pp. (1955).

This new iron vanadate,  $3\text{FeO} \cdot \text{V}_2\text{O}_5 \cdot 3\text{V}_2\text{O}_4$ , occurs in four mines. It is a major constituent in the Pitche group where in hand specimen it is massive gray with a bluish tarnish; under the microscope it is in hexagonal plates. Associated minerals are hematite and chalcopyrite. It is a minor constituent (a) at Fish Hook Bay, in laths in dolomite; (b) at the Nicholson No. 2 mine where a bladed boxwork of nolanite and dolomite contains chalcopyrite, galena, and other sulfides, also in veins with pitchblende and sulfides; (c) in veins at the Ace mine, associated with pitchblende and ilmenite. Structural data for the mineral have been published by Barnes and Qurashi, *Am. Mineral.*, **37**, 420–421 (1952). A complete account is to be published in the *Am. Mineralogist* by Robinson, Fahey, and Schaller. The name is for Thomas B. Nolan, Assistant Director, U. S. Geological Survey (private communication from W. T. Schaller).

M. F.

### Cardosonite

ISIDORO ASENSIO AMOR, Investigacion por Rayos X de algunos fosfatos de origen secundario hallados en "Puerto de Son" (Coruna). Cardosonite, un nuevo miembro de la serie de la Dufrenita. *Estudios geol., Inst. invest. geol.* "Lucas Mallada" (Madrid), **13**, No. 25, 43–50 (1955) (from a translation kindly made by Daniel E. Appleman).

A clear green mineral is associated with eosphorite, evansite, and smoky quartz. Qualitative analysis showed Ca, Mg, and Mn, but no ferrous iron. Quantitative analysis (incomplete for lack of material) gave  $\text{P}_2\text{O}_5$  24.76,  $\text{Fe}_2\text{O}_3$  54.07,  $\text{H}_2\text{O}$  9.21%. The  $x$ -ray powder data are given; they agree fairly well with those obtained on dufrenite from Hirsch-

berg, Westphalia. The differences in chemical composition and in exterior appearance (compact, massive, without fibrous structure) are considered to be sufficient to warrant a new name.

The name is for Martin Cardoso, who had previously described the associated evansite and esphorite.

DISCUSSION: Insufficient basis for a new name.

M. F.

### Absite

A. W. G. WHITTIE, Absite—a new mineral related to brannerite. *South Australia Dept. Mines, Mining Review No. 97* for 1952, pp. 99–106 (1954); also partial description in *S. Australia Geol. Survey, Bull. No. 30*, 79–83, 126–151 (1954).

A chemical analysis gave  $\text{TiO}_2$  35.13,  $\text{UO}_3$  31.83,  $\text{ThO}_2$  12.81,  $\text{Sc}_2\text{O}_3$  0.19,  $\text{Ce}_2\text{O}_3$  1.43,  $\text{Y}_2\text{O}_3$  etc. 3.71,  $\text{ZrO}_2$  0.38,  $\text{Fe}_2\text{O}_3$  1.37,  $\text{PbO}$  2.79,  $\text{P}_2\text{O}_5$  0.13,  $\text{H}_2\text{O}^-$  2.54,  $\text{H}_2\text{O}^+$  7.41; sum 99.72%. Cr, V, Be, Mn, Ca, Mg, Ta, and Nb were absent. The analysis suggests the formula  $2 \text{UO}_3 \cdot \text{ThO}_2 \cdot 7 \text{TiO}_2 \cdot 5 \text{H}_2\text{O}$ . Absite does not fuse when heated to redness, but expands and splits. The mineral is readily decomposed by  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ . Non-fluorescent.

It is yellow to yellow-brown or brownish olive-green. Hardness of purest samples 5 to 6, G. 4.0 to 4.2. Luster resinous on fresh fracture to dull on weathering. Fracture irregular; very brittle. Optically isotropic,  $n$  somewhat variable with degree of weathering, but mainly  $1.96 \pm .01$ .

X-ray study by K. Norrish shows the mineral to be amorphous, presumably metamict, the only lines observed being weak ones corresponding to the presence of a little rutile. When heated at  $900^\circ$ , the mineral gives an x-ray pattern, the strongest lines being at 3.43 and 4.79 kX.

Absite occurs in irregular grains in a zone of brecciated rocks ranging from adamellite to granodiorite at Crookers Well, South Australia. It also occurs in rutile-bearing quartz veins, sometimes in forms 5–10 cm. in size that simulate hexagonal or triclinic crystals.

The mineral is considered to be related to brannerite, differing in containing no  $\text{UO}_2$ , in containing  $\text{ThO}_2$ , and more  $\text{H}_2\text{O}$ . It is stated that the x-ray data on heated material are similar to those given by heated brannerite.

The name is an abbreviation of air-borne scintillometer, by which means the deposit was discovered.

DISCUSSION: An unnecessary name for thorian brannerite.

M. F.

### Wairakite

A. STEINER, Wairakite, the calcium analogue of analcime, a new zeolite mineral. *Mineral. Mag.*, **30**, 691–698 (1955).

D. S. COOMBS, X-ray observations on wairakite and non-cubic analcime. *Mineral. Mag.*, **30**, 699–708 (1955).

Wairakite occurs in tuffaceous sandstones and breccias, vitric tuffs and welded tuffs in drill cores from levels 600 to 2890 ft. and in rocks ejected by steam from some of the drill holes. In drill cores it is fine-grained, replacing andesine and filling cavities. In some of the ejected rocks, it occurs as megascopic veinlets, 0.5 to 0.25 mm. thick, which may be lined with subhedral crystals up to 15 mm. across, showing partial octahedron and trepezohedron faces.

Analysis by J. A. Ritchie of pure material gave  $\text{SiO}_2$  55.9,  $\text{Al}_2\text{O}_3$  23.0,  $\text{CaO}$  11.7,  $\text{SrO}$  0.05,  $\text{Na}_2\text{O}$  1.06,  $\text{K}_2\text{O}$  0.16,  $\text{Cs}_2\text{O}$  0.017,  $\text{Rb}_2\text{O}$  0.0003,  $\text{H}_2\text{O}^-$  0.15,  $\text{H}_2\text{O}^+$  8.35; sum 100.39%.



which corresponds closely to  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , which corresponds to the formula of analcime with Ca replacing  $\text{Na}_2$ . Study of the literature shows few analysis intermediate between analcime and wairakite. The mineral loses 4.23% from  $110^\circ$  to  $380^\circ \text{C}$ ., 4.09% from  $380^\circ$  to  $800^\circ$ , and 0.03% above  $800^\circ$ . It fuses at  $2\frac{1}{2}$ . Gelatinizes with HCl.

Wairakite is colorless to white, luster vitreous to nearly dull. G. 2.26, hardness  $5\frac{1}{2}$ -6. The mineral is brittle. Two sets of partings (?) intersecting at right angles and parallel to two sets of twinning lamellae were observed under the microscope. The mineral is biaxial and shows no isotropic patches (in contrast to birefringent analcime),  $\alpha$  (near  $b$ ) 1.498,  $\gamma$  (near  $c$ ) 1.502, both  $\pm 0.001$ ,  $2V_\gamma$  variable  $70^\circ$  to  $105^\circ$ , average near  $90^\circ$ , dispersion weak  $r > v$  about  $\gamma$ .

The x-ray powder pattern shows doubling of many lines of the analcime pattern indicating departures from cubic symmetry and corresponding to a cell with maximum and minimum dimensions of about 13.68 Å and 13.56 Å. Weissenberg photographs of optically oriented sections show wairakite to be monoclinic, space group  $Ia$  or  $I2/a$ ,  $a$   $13.69 \pm .02$ ,  $b$  13.68,  $c$  13.56 Å,  $\beta$   $90.5^\circ$ ; the unit cell contains 8  $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ . The cell is pseudo-cubic and pseudo-tetragonal.

The mineral is of hydrothermal origin. The waters in the drill holes are alkaline and temperatures measured range from  $200^\circ$  to  $250^\circ \text{C}$ . Calculated hydrostatic pressures are 55 to 265 atmospheres. There is no evidence to suggest that wairakite has formed from analcime by ion exchange.

The name is for the locality, Wairakei, in the central part of the North Island, New Zealand, about 4 miles from Lake Taupo.

M. F.

### Isokite

T. DEANS AND J. D. C. MCCONNELL, Isokite,  $\text{CaMgPO}_4\text{F}$ , a new mineral from Northern Rhodesia. *Mineral. Mag.*, **30**, 681-690 (1955).

Isokite occurs as fibrous spherulites, commonly 0.5 to 1 mm. in diameter, rarely up to 2 or 3 mm. in diameter, in ankeritic rocks of a carbonatite plug at Nkumbwa Hill, 15 miles east of Isoka (pronounced Isōka). Associated minerals include strontian fluorapatite, pyrite, ilmenite, barite, monazite, pyrochlore, and sellaite. Analysis by R. Pickup gave  $\text{CaO}$  30.72,  $\text{SrO}$  1.65,  $\text{BaO}$  0.21, rare earths 0.16,  $\text{MgO}$  21.58,  $\text{FeO}$  0.49,  $\text{MnO}$  0.13,  $\text{P}_2\text{O}_5$  37.76,  $\text{F}$  9.55,  $\text{H}_2\text{O}$  below  $300^\circ$  0.26,  $\text{H}_2\text{O}$  above  $300^\circ$  0.46,  $\text{CO}_2$  1.02, acid insol. 0.10; sum 104.09 less ( $\text{O}=\text{F}_2$ ) 4.02, 100.07%. After deduction of 2.14% ankeritic dolomite and 0.99% fluorapatite, this corresponds closely to  $\text{CaMgPO}_4\text{F}$ . The mineral dissolves slowly in cold HCl, rapidly in warm acids.

Isokite is colorless to buff or pinkish, luster silky to slightly pearly. G. 3.27 for crystalline plates, down to 3.15 for fibrous material, 3.29 calcd. from x-ray data. Hardness above 4, probably 5. Fluoresces blue under longwave (3650 Å) ultra-violet light. Optically biaxial, positive,  $\alpha$  1.590,  $\beta$  1.595,  $\gamma$  1.615 (all  $\pm .002$ ),  $2V$   $51$ - $51\frac{1}{2}^\circ \pm 2^\circ$  (Universal stage),  $\gamma=b$ ,  $\alpha:c = +32^\circ$ , dispersion  $r > v$ ,  $\text{Bx}_a$  normal to the cleavage plates.

The plates show the forms (001), (100), (101), (10 $\bar{1}$ ), and (102); angles measured under the microscope agree well with those from the x-ray data. Weissenberg and oscillation photographs show isokite to be monoclinic, space group  $C2/c$  (test for pyroelectricity negative),  $a$  6.52,  $b$  8.75,  $c$  7.51 Å. (all  $\pm 0.05$  Å),  $\beta$   $121^\circ 28' \pm 12'$ .  $a:b:c = 0.745:1:0.858$ . There is a very good cleavage, (010). X-ray powder data are given. Isokite is isostructural with durangite ( $\text{NaAlAsO}_4\text{F}$ ), tilasite ( $\text{CaMgPO}_4\text{F}$ ), and sphene [ $\text{CaTiSiO}_4(\text{O}, \text{OH}, \text{F})$ ].

The name is for the locality.

M. F.

## DISCREDITED MINERALS

## Alvarolite (= Mangantantalite)

ELYSIARIO TAVORA, X-ray diffraction powder data for some minerals from Brazilian localities. *Anais Acad. Brasileira Cienc.*, **27**, 7-29 (1955).

X-ray powder data on type material (see *Am. Mineral.*, **39**, 159 (1954)), showed alvarolite to be identical with mangantantalite.

M. F.

## Ribeirite (= Yttrian zircon)

E. TAVORA, *op. cit.*

X-ray powder data on type material (see *Am. Mineral.*, **39**, 159 (1954)) gave a weak pattern with 10 lines corresponding closely to the strongest lines of zircon. The heated sample gave a sharp pattern corresponding closely to that of zircon.

M. F.

## Curtisite (= Idrialite)

K. TUČEK AND J. KOUŘIMSKÝ, The occurrence of curtisite in Czechoslovakia and its identity with idrialine. *Rozpravy česk. Akad. Věd.*, **63**, No. 3, 1-18 (1953) (English summary).

A hydrocarbon found in fissures in andesite at Ordějov, Moravia, had  $G. 1.225$ ,  $\alpha 1.557 \pm .001$ ,  $\beta 1.738 \pm .001$ ,  $\gamma$  above 1.83. The optical data suggest monoclinic symmetry. The optics and x-ray powder patterns are identical with those of curtisite from Skaggs Springs, Cal. (Wright and Allen, *Am. Mineral.*, **15**, 169-173 (1930)) and idrialite from Idria, Yugoslavia (Dana's System, 6th Ed., p. 1013).

The name idrialite has priority.

M. F.

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Corrections

A number of typographical errors appear in the paper by E. G. Zies and H. E. Merwin in the article "Analysis of Hamley bornite from South Australia," in the November-December issue, 1955, pages 1002 and 1003. *Page 1002, Table 1, last column*: The footnote reference for the third and fourth figures down should be *f* instead of *b*. The column total should be 99.90, instead of 99.80.

*Page 1003, Table*: The total of the second column should be 99.91, instead of 99.51.

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